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Sodium-catalyzed Side Chain Aralkylation of Alkylbenzenes with Styrene¹

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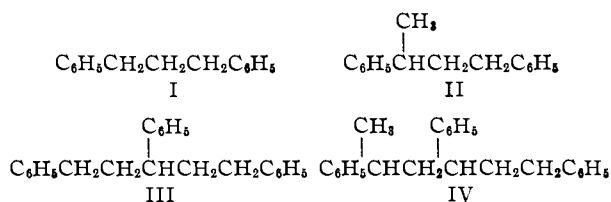
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Toluene and ethylbenzene react with styrene in the presence of sodium to form monoadducts, 1,3-diphenylpropane (I) and 1,3-diphenylbutane (II) and diadducts 1,3,5-triphenylpentane (III) and 1,3,5-triphenylhexane (IV), respectively. The yield of monoadducts can be increased by the presence of promoters, such as benzylsodium, anthracene or sodium isopropoxide. Isopropylbenzene requires the presence of promoters in order to react with styrene to form mono- and diadducts; in the absence of promoters a polymeric type of material is produced. A mechanism is postulated to explain the function of the promoters.

The literature on the behavior of styrene toward alkylbenzenes in the presence of sodium is controversial. Wegler and Pieper³ reported that styrene underwent polymerization when treated with sodium in the presence of toluene; they did not give, however, a detailed description of their experimental conditions. Frank and Swinehart⁴ claimed that ethylbenzene reacts with styrene in the presence of finely divided sodium to form 1,3-diphenylbutane as the principal product.

As a continuation of the study of the side chain alkylation of alkylbenzenes in the presence of sodium-organosodium catalysts^{1,5-7} the reaction of styrene with toluene, ethylbenzene and isopropylbenzene was investigated. Most of the experiments were carried out at temperatures varying from 110-125° with efficient stirring using as catalyst sodium as such or promoted by the addition of small amounts of benzylsodium, anthracene or sodium isopropoxide.

It was found that toluene and ethylbenzene react with styrene in the presence of sodium to form monoadducts, 1,3-diphenylpropane (I) and 1,3-diphenylbutane (II), and diadducts, namely 1,3,5-triphenylpentane (III) and 1,3,5-triphenylhexane (IV), respectively.



In addition to these compounds high boiling residues were obtained, which probably resulted from the condensation of the respective alkylbenzenes with three or more molecules of styrene. The yield of monoadduct can be increased, in the case of toluene, from 20 to 40%, and of the diadduct from 23 to 29% if 3 mole per cent. of benzylsodium, based on styrene, or 13%, based on sodium, is added. A similar increase in yield of mono- and diadduct was observed when benzylsodium promoter was added

(1) Paper XV of the series Base-catalyzed Reactions. For paper XIV see H. Pines and L. Schaap, *THIS JOURNAL*, **80**, 4378 (1958).

(2) Vladimir N. Ipatieff Postdoctoral Fellow.

(3) R. Wegler and G. Pieper, *Ber.*, **83**, 6 (1950).

(4) C. E. Frank and J. S. Swinehart, U. S. Patent 2,761,886, September 4, 1956.

(5) H. Pines, J. A. Vesely and V. N. Ipatieff, *THIS JOURNAL*, **77**, 554 (1955).

(6) H. Pines and V. Mark, *ibid.*, **78**, 4318 (1956).

(7) L. Schaap and H. Pines, *ibid.*, **79**, 4467 (1957).

to ethylbenzene. Anthracene and sodium isopropoxide also act as promoters for the phenethylation reaction (Table I).

TABLE I

REACTION OF STYRENE WITH ALKYLAROMATIC IN THE PRESENCE OF SODIUM

The experiments were made, unless otherwise indicated, using 2.0 g. (0.09 g. at.) of sodium, 0.01 mole of promoter, 34.5 g. (0.33 mole) of styrene and about one mole of alkylbenzene.

Expt.	Alkylbenzene R	Promoter ^a	Conditions °C.	Hr.	Yield, % ^b	Mono- adduct Un- satn., % ^c	Diad- duct yield, % ^b	Resi- due, g. ^d
1	CH ₃	..	110	1.5	21		23	15
2	CH ₃	A	50	2.0	1		29	28
3	CH ₃	A	80	1.3	12	2.4	39	12
4	CH ₃	A	114	1.3	40	4.3	29	7
5	CH ₃	A ^e	112	2.0	22	0	36	12
6	CH ₃	A ^f	112	1.5	8	2.9	28	20
7	CH ₃	B	112	2.0	33	1.2	26	12
8	CH ₃	C	113	1.5	41	0.6	28	8
9	C ₂ H ₅	..	115	1.5	12	0	16	22
10	C ₂ H ₅	A	115	1.5	22	0.8	35	13
11	C ₂ H ₅	A ^g	115	3.5	49	0	28	20
12	C ₂ H ₅	C	115	1.5	43	0	20	12
13	<i>i</i> -C ₃ H ₇	..	125	1.0				35
14	<i>i</i> -C ₃ H ₇	A	125	1.5	9	0	29	16
15	<i>i</i> -C ₃ H ₇	C	125	1.3	14	0	29	13
16	<i>i</i> -C ₃ H ₇	E	125	1.0	3	0.5	14	23
17	<i>i</i> -C ₃ H ₇	E ^h	125					No reaction

^a A = *o*-chlorotoluene; B = anthracene; C = sodium isopropoxide, the corresponding amount of isopropyl alcohol was added; E = sodium hydroxide, the corresponding amount of water was added. ^b Based on styrene charged. ^c The unsaturation was determined by either hydrogen number or bromine number. ^d The weight includes the weight of residue and that of styrene obtained from the thermal decomposition of the residue in some of the distillations. ^e One gram (0.05 g. at.) of sodium and 0.005 mole of promoter were used. ^f About 0.5 (0.02 g. at.) of sodium and 0.002 mole of promoter were used. ^g The following amounts of reagents were used: ethylbenzene 400 ml., sodium 10 g. (0.45 g. at.), *o*-chlorotoluene 7.1 g. (0.06 mole) and 182 g. (1.75 moles) of styrene. ^h Sodium isopropoxide was prepared by treating 5.7 g. (0.09 mole) of isopropyl alcohol with 2.0 g. (0.09 g. at.) of finely divided sodium; excess of sodium as a catalyst was not used.

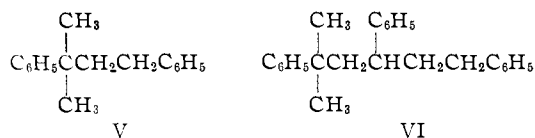
Isopropylbenzene, unlike toluene and ethylbenzene, does not react with styrene in the presence of sodium alone to form mono- and diadducts. The product of the reaction consisted of a very viscous material composed probably of polymers of styrene or of products of interaction of isopropylbenzene

TABLE II
 PHYSICAL CONSTANTS AND ANALYSES OF PHENETHYLATED ALKYL BENZENES, C₆H₅R

R =	Adducts from Kind	Compound A = C ₆ H ₅	°C.	B.p. Mm.	n _D ²⁰	d ₄ ²⁰	Formula	Calculated C, %	H, %	Found C, %	H, %
CH ₃	Mono-	ACCCA (I) ^a	103-107	2	1.5577	0.9757	C ₁₅ H ₁₆	91.85	8.15	91.91	8.12
CH ₃	Di-	ACCCCA (III) ^b	179.2 ^c	0.7	1.5768	1.0172	C ₂₃ H ₂₄	91.95	8.05	92.03	7.81
C ₂ H ₅	Mono-	ACCCA (II) ^{a,b}	105	1	1.5520	0.9661	C ₁₆ H ₁₈	91.37	8.63	91.43	8.47
C ₂ H ₅	Di-	ACCCCA (IV) ^b	179.5 ^c	0.7	1.5714	1.0087	C ₂₄ H ₂₆	91.66	8.34	91.67	8.07
<i>i</i> -C ₃ H ₇	Mono-	ACCCA (V) ^b	118.6 ^c	1.0	1.5507	0.9675	C ₁₇ H ₂₀	91.01	8.99	90.91	8.88
<i>i</i> -C ₃ H ₇	Di-	ACCCCA (VI) ^b	184 ^c 209.2 ^c	1.4 3.1	1.5700	1.0064	C ₂₅ H ₂₈	91.41	8.59	91.70	8.72

^a Infrared spectra were identical with that reported by K. T. Serjan, I. A. Goodman and W. J. Yankauskas, Nat. Advisory Committee for Aeronautics Technical Note 2557 (1951). These authors reported for I: b.p. 299° at 760 mm., n_D²⁰ 1.5594, d₄²⁰ 0.9800; for II: b.p. 303° at 760 mm., n_D²⁰ 1.5523, d₄²⁰ 0.9698. ^b Infrared spectra were identical with those of synthesized hydrocarbons. ^c Determined on a modified Cottrell apparatus [F. G. Cottrell, THIS JOURNAL, 41, 721 (1919)]. The apparatus was modified by Universal Oil Products Co., Des Plaines, Ill.

with several molecules of styrene. In the presence of any of the above indicated promoters interaction of isopropylbenzene with styrene takes place to yield monoadduct 2-methyl 2,4-diphenylbutane(V) and diadduct 2-methyl-2,4,6-triphenylhexane (VI); some higher boiling compounds also were produced.



Sodium hydroxide acts to a smaller extent also as promoter for this reaction, while sodium isopropoxide is inert.

The mono- and diadducts obtained from the reaction of styrene with the various alkylbenzenes were identified by comparing their physical constants and infrared spectra with the synthetically prepared hydrocarbons (Table II). The monoadduct fraction of some of the experiments contained, according to bromine number determination, less than 5% of unsaturation. The fractions containing unsaturated hydrocarbons were selectively hydrogenated before submitting them to infrared spectral analyses.

During the distillation of the diadduct, especially when the concentration of the high boiling residue was high, part of the latter was decomposed to generate styrene. The amount of styrene thus obtained was added to the weight of the residue.

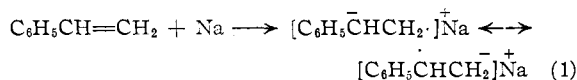
The effect of temperature upon the phenethylation of toluene in the presence of sodium-benzylsodium catalyst was studied. At 50° 1 and 29%, at 80° 12 and 39% and at 115° 40 and 29% of mono- and diadducts were formed, respectively. The amount of catalyst also has an effect upon the yields of mono- and diadducts. When the molal ratio of styrene:sodium (g. atom):benzylsodium was equal to 1:0.26:0.03 the yields of mono- and diadducts were 40 and 29%, respectively; the yield of monoadduct decreased sharply while that

of the residue increased, when the concentration of the catalyst was diminished (expt. 4 and 5).

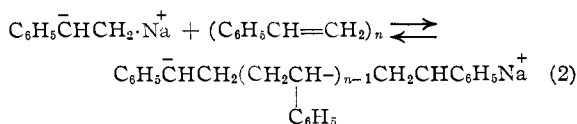
Discussion of Results

Unlike the base-catalysed alkylation of toluene and ethylbenzene with alkenes,⁵⁻⁷ the phenethylation of these alkylaromatics in the presence of sodium does not require the assistance of promoters. The addition compound between styrene and sodium acts as a chain initiator for the phenethylation reaction. In the presence, however, of a chain promoter, such as benzylsodium or sodium isopropoxide, the reaction proceeds more selectively and the yield of monoadduct produced is much higher. In the case of isopropylbenzene the presence of a promoter is essential, since without it only high boiling polymeric compounds are produced.

The results obtained can be explained by assuming that styrene reacts with sodium by a single electron transfer to form both a carbanion and a free radical, according to the equation

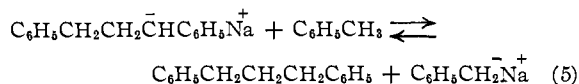
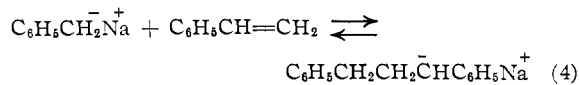
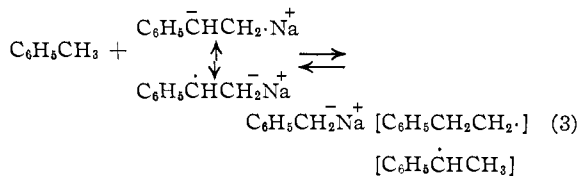


The organosodium free radical thus produced may add *via* free radical to styrene to form a polymeric material. This probably happens when the reaction is carried out in the presence of methylcyclohexane solvent or in the presence of isopropylbenzene. In the presence of the latter the polymeric material was very viscous while in the presence of methylcyclohexane it was solid, which indicates its higher molecular weight. The polymerization reaction could be written as

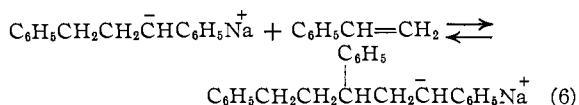


When the reaction was carried out, however, in the

presence of toluene, the latter underwent metalation and the phenethylation reaction was initiated



It may also be possible for the diphenylpropylcarbanion produced in (4) to add to another molecule of styrene to form a diadduct



Reaction 3 is energetically favorable since the primary benzylic carbanion is more stable than a secondary benzylic carbanion or a primary resonance non-stabilized carbanion.⁶ Reaction 4, although energetically less favorable, occurs readily in the presence of an excess of toluene, as indicated in equation 5. The di- or polyadduct formation may occur directly, as indicated by equation 6; the two carbanions indicated in this equation are energetically equal.

The free radicals which were assumed to be formed, as indicated by equations 1, 2 and 3, could undergo one of the usual types of termination reactions.

The yield of monoadduct produced from toluene was higher than that from ethylbenzene and none was produced from isopropylbenzene. This could be explained by the relative acidities of the alkylbenzenes, which decrease from $\text{C}_6\text{H}_5\text{CH}_3 > \text{C}_6\text{H}_5\text{-C}_2\text{H}_5 > \text{C}_6\text{H}_5\text{CH}(\text{CH}_3)_2$. The chain transfer reaction, as indicated by equation 3, is therefore more favorable for toluene, less favorable for ethylbenzene and much less for isopropylbenzene. For that reason in the latter case the competing, free radical addition reaction, would be preferred.

The more extensive polymerization of styrene in the presence of methylcyclohexane than in isopropylbenzene could be explained by a more favorable chain termination reaction in the latter case.

The beneficial effect of benzylna or sodium isopropoxide upon the yield of monoadduct produced probably could be explained by a facilitation of metalation of alkylbenzenes as indicated by equation 3. Morton and co-workers⁸⁻¹⁰ found that the metalation of alkylbenzenes is facilitated by the presence of metal oxides such as sodium oxide, potassium oxide,^{8,9} alkoxides,¹⁰ etc.

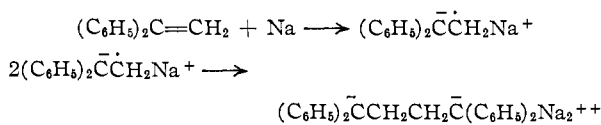
Evidence for the formation of organosodium free radicals by one-electron transfer between styrene

(8) C. E. Claff, Jr., and A. A. Morton, *J. Org. Chem.*, **20**, 440, 981 (1955).

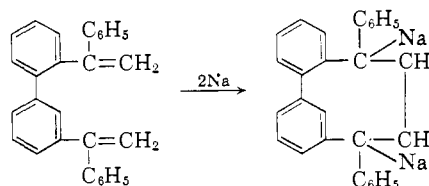
(9) A. A. Morton, C. E. Claff, Jr., and F. W. Collins, *ibid.*, **20**, 478 (1955).

(10) A. A. Morton and E. F. Claff, *THIS JOURNAL*, **74**, 4056 (1952).

and sodium (equation 1) has its precedents in the literature. Thus the dimerizing addition of 1,1-diphenylethylene^{11,12} was explained as¹³



Single electron transfer reaction also was used to explain the cyclization of styrene derivatives.¹⁴



Experimental Part

Procedure.—Freshly cut sodium (2.0 g., 0.09 g. at.) was added into the flask containing 140 ml. of the desired alkylbenzene. When required, about 0.01 mole of a promoter was added to the alkylbenzene. The content of the flask was heated under a blanket of nitrogen under 5000–6000 r.p.m. stirring. When the desired temperature was reached and the sodium was finely divided, 34.5 g. of freshly distilled styrene, dissolved in 35 ml. of the alkylbenzene, was added dropwise; when phenethylation reaction took place, the color of the reaction mixture turned dark red.

The reactants then were cooled, the catalyst was destroyed by the addition of 10 ml. of ethanol. The reaction mixture was washed with dilute hydrochloric acid, followed by aqueous sodium carbonate and dried. The unreacted alkylaromatics were flash distilled, and the reaction product was distilled under reduced pressure, using a modified Vigreux column.

The fractions which distilled within mono- and diadduct ranges were combined respectively and when bromine number indicated the presence of olefins, selectively hydrogenated using *n*-pentane as a solvent and copper–chromite as a catalyst. The hydrogenation was made under an initial hydrogen pressure of 120 atmospheres and at 120°. Under these conditions only the olefinic double bonds were hydrogenated.

The selectively hydrogenated mono- and diadducts of some of the more representative experiments were distilled on a Podbielniak whirling band column.¹⁵ The phenethylated compounds were analyzed and their infrared spectra compared with those of synthetically prepared hydrocarbons.

Synthesis of Hydrocarbons. 1,3,5-Triphenylpentane (III). 1,3,5-Triphenyl-3-pentanol.—To a Grignard solution prepared from 26.7 g. (0.14 mole) of β -phenylethyl bromide and 3.5 g. (0.14 g. at.) of magnesium in 150 ml. of ether, was added 28.0 g. (0.13 mole) of benzylacetophenone, m.p. 71–72°. The ketone was synthesized according to the method described in the literature.¹⁶ The Grignard solution was refluxed for 0.5 hour and worked up in the usual manner. About 47% of the benzylacetophenone was recovered. The 1,3,5-triphenyl-3-pentanol on distillation underwent a partial dehydration; b.p. 195–207° at 1.5 mm., n_D^{20} 1.5921, yield 18.9 g. or 45–47% of the theoretical.

Anal. Calcd. for $\text{C}_{23}\text{H}_{24}\text{O}$: C, 87.30; H, 7.65. For $\text{C}_{23}\text{H}_{22}$: C, 92.57; H, 7.43. Found: C, 90.90; H, 7.56.

1,3,5-Triphenylpentane (III).—The mixture of the carbinol and the olefins described above, 17.2 g., dissolved in 30 ml. of benzene, was hydrogenolyzed at 170° using 1.7 g.

(11) W. Schlenk and E. Bergmann, *Ann.*, **463**, 1 (1928); **479**, 58 (1930).

(12) W. Schlenk, J. Appenrodt, A. Michael and A. Thal, *Ber.*, **47**, 473 (1914).

(13) G. E. Coates in "Organic-Metallic Compounds," Methuen and Co., Ltd., London, 1956, p. 17.

(14) G. Wittig and W. Stiltz, *Ann.*, **598**, 53 (1956).

(15) Podbielniak, Inc., Chicago, Ill.

(16) L. W. Covert, R. Connor and H. Adkins, *THIS JOURNAL*, **54**, 1651 (1932).

TABLE III
 INFRARED SPECTRA OF PHENYLALKANES

$\begin{array}{c} \text{C} \\ \\ \text{Ar}-\text{C}-\text{C}-\text{C}-\text{Ar} \\ \\ \text{C} \end{array}$ V ^b	$\begin{array}{c} \text{Ar} \\ \\ \text{Ar}-\text{C}-\text{C}-\text{C}-\text{C}-\text{Ar} \\ \\ \text{C} \end{array}$ III ^c	$\begin{array}{c} \text{C} \quad \text{Ar} \\ \quad \\ \text{Ar}-\text{C}-\text{C}-\text{C}-\text{C}-\text{Ar} \\ \quad \\ \text{C} \quad \text{C} \end{array}$ IV ^c	$\begin{array}{c} \text{C} \quad \text{Ar} \\ \quad \\ \text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{Ar} \\ \quad \\ \text{C} \quad \text{C} \end{array}$ VI ^c
Wave length, μ^a			
3.28w	3.26w	3.26w	3.28w
3.30s	3.29s	3.30s	3.30s
3.41s	3.41s	3.43s	3.42s
3.50w	3.50w	3.46w	3.50w
3.85w	3.85w	3.68w	
4.29w	4.24w	4.40w	4.40w
	4.39w		
5.12m	5.12m	5.13m	5.12m
5.35m	5.35m	5.35m	5.35m
5.55m	5.55m	5.55m	5.53m
5.74m	5.74m	5.74m	5.72m
6.00w	6.00w	6.00w	6.00w
6.21s	6.21s	6.22s	6.21s
6.29w			
6.49w			
6.68s			
6.76w			
6.86s			
6.91m	6.92m	6.95w	6.93m
7.21s	7.28m(s)	7.28m(s)	7.20m
			7.29s
7.31s	7.39m	7.39w	7.39w
7.48w	7.49w	7.53w	7.48w
7.65m	7.60w	7.66w	
	7.66w		
7.73w		7.75w	7.72m
7.80w			7.86w
7.99m	8.08w	7.93w	8.01w
8.30m	8.26w		
8.34w			8.36m
8.46w	8.45w	8.48w	8.45w
8.62m	8.63m	8.65m(s)	8.62m
8.76w	8.98w	8.98w	8.71w
9.05m	9.18m	9.13w	9.06m
9.25w	9.24w	9.27w	9.26s
9.30s		9.36w	9.40w
9.66s	9.66s	9.70s	9.66s
9.95w	9.89w	9.92w	9.92w
	10.00w	10.05w	10.12w
10.19w	10.17w	10.18w	
10.61w	10.35w	10.35w	10.35w
10.79m			10.70w
11.01m(s)	11.04m(s)	11.05m(s)	11.05m(s)
11.09w			
11.51w	11.62w	11.40w	
11.88m	11.87m	11.92m	11.90m
12.24w		12.20w	12.20w
12.41w	12.67w	12.40w	12.40w
		12.70w	12.70w
13.10s	13.04s	13.13s	13.08s
13.32s	13.40s	13.32s	13.15s
14.1-14.4s	14.26s	13.48s	13.30s
		14.26-14.34s	14.2-14.4s
15.00w	15.00w	15.00w	14.98w

^a The peaks are referred to as: s = strong, m = medium, w = weak. ^b 0.041-mm. sodium chloride cell. ^c 0.073-mm. cell; the hydrocarbon was dissolved in equal volume of carbon disulfide.

of copper chromite as catalyst¹⁷ and initial hydrogen pressure of 150 atmospheres. Compound III thus obtained boiled¹⁸ at 180° (0.7 mm.) or at 205.5° (2.5 mm.), n_{D}^{20} 1.5770, d_4^{20} 1.0178, yield 80%; literature¹⁹ b.p. 170–172° at 0.5 mm.

Anal. Calcd. for $C_{23}H_{24}$: C, 91.95; H, 8.05. Found: C, 92.03; H, 8.05.

1,3,5-Triphenylhexane (IV). 1,3,5-Triphenyl-3-hexanol.—To 13 ml. of 1.82 *N* ether solution of β -phenylethylmagnesium bromide was added 4.3 g. (0.019 mole) of 3-phenylbutyrophene, m.p. 72.5–73°, in 40 ml. of ether. The ketone was prepared according to Kohler.²⁰ The carbinol, 4.3 g., yield 67%, distilled at 206–208° at 1 mm., n_{D}^{20} 1.5730 (new compound).

Anal. Calcd. for $C_{24}H_{26}O$: C, 87.22; H, 7.93. Found: C, 87.57; H, 7.85.

1,3,5-Triphenylhexane (IV) was prepared by hydrogenating 7.3 g. of the carbinol, according to the method described for the preparation of compound III. Compound IV distilled at 156–159° 0.01 mm., n_{D}^{20} 1.5707, d_4^{20} 1.0104 (new compound).

Anal. Calcd. for $C_{24}H_{26}$: C, 91.66; H, 8.34. Found: C, 91.47; H, 8.17.

1,3,5-Triphenyl-5-methylhexane (VI). 1,3,5-Triphenyl-5-methyl-3-hexanol was prepared by treating a Grignard solution obtained from 37 g. (0.22 mole) of neophyl chloride²¹ and 5.5 g. (0.22 g. at.) of magnesium with 41.5 (0.20 mole) of benzylacetophenone, m.p. 71–72°; after refluxing for 7 hours and the usual work up, 63% of the benzylacetophenone was recovered. The product of the reaction contained *t*-butylbenzene, 38% based on neophyl chloride charged. The condensation product, 28.5 g., b.p. 205–227° at 2 mm., n_{D}^{20} 1.5829–1.5846, consisted of a mixture of the desired carbinol and its dehydration product. According to hydrogen number the olefinic hydrocarbons present in this fraction amounted to 70%.

1,3,5-Triphenyl-5-methylhexane (VI) was obtained by hydrogenating 27.5 g. of the above mixture using copper-chromite as a catalyst, according to the procedure described above. Compound VI thus obtained boiled¹⁸ at 210.6° and 3.1 mm., n_{D}^{20} 1.5701, d_4^{20} 1.0060 (new compound).

Anal. Calcd. for $C_{25}H_{28}$: C, 91.41; H, 8.59. Found: C, 91.64; H, 8.52.

1,3-Diphenyl-3-methylbutane (V). 1,3-Diphenyl-3-methyl-1-butanol.—Freshly distilled benzaldehyde (42.5 g., 0.4 mole) was added to a refluxing Grignard solution obtained from 51 g. (0.3 mole) of neophyl chloride²¹ and 7.3 g. (0.3 g. at.) of magnesium in 100 ml. of ether. The new alcohol, which was obtained in 69% yield (50 g.), distilled at 180–186° at 2 mm. After recrystallization from aqueous methanol it melted at 92°.

Anal. Calcd. for $C_{17}H_{20}O$: C, 84.93; H, 8.38. Found: C, 85.62; H, 8.52.

1,3-Diphenyl-3-methylbutane (V).—The alcohol which was described above (45 g., 0.19 mole) was dissolved in 100 ml. of benzene and hydrogenated at 185° in the presence of copper-chromite under an initial hydrogen pressure of 110 atm. Compound V thus obtained in 94% yield distilled at 115–119° at 1.5 mm., n_{D}^{20} 1.5507, d_4^{20} 0.9879 (new compound).

Anal. Calcd. for $C_{17}H_{20}$: C, 91.01; H, 8.99. Found: C, 91.22; H, 9.07.

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(18) Determined on a Cottrell boiling point apparatus; ref. Table 2, footnote c.

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