2. The silver salt of hydroxynaphthoquinone reacts with alkyl halides to give varying proportions of α-naphthoquinone-ether and β-naphthoquinone ether, the relative amount of the former increasing somewhat as the reactivity of the alkyl halide increases. The *p*-quinone ether is considered to be formed by normal replacement, while the formation of the *o*-quinone ether is regarded as involving 1,4 addition. The silver salt of chloro-hydroxynaphthoquinone reacts only in the first manner, giving the *p*-quinone ether.

3. Alkylation of hydroxynaphthoquinone with an alcohol and a mineral acid, or with diazomethane, yields exclusively the 2-alkoxy-1,4-naphthoquinone.

4. Consideration of these reactions, and of the behavior of the two types of ethers towards acid hydrolyzing agents, leads to the conclusion that in solution hydroxynaphthoquinone consists of a mixture of tautomers, with the orthoquinone form present in extremely small concentration.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE COUPLING ACTION OF THE GRIGNARD REAGENT
III. THE QUESTION OF THE FORMATION OF 1,2,3-TRIPHENYLPROPANE AND SIMILAR HYDROCARBONS IN THE COUPLING REACTIONS OF THE BENZYL HALIDES

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Introduction

In a study of the action of the Grignard reagent on alkyl halides, Späth[2] obtained products whose formation he attributed to a coupling reaction involving the combination of free alkyl and alkylene radicals assumed to exist as intermediates. By the action of various Grignard reagents on the benzyl halides he prepared a compound which he identified as 1,2,3-triphenylpropane (I). From ethylmagnesium bromide and benzyl chloride he obtained similarly a liquid which possessed the properties of α-ethyl-α,β-diphenylethane (II). Phenylmagnesium iodide with *p*-methoxybenzyl bromide gave a resinous solid to which Structure III was assigned.

Späth assumed that the first step in these reactions was the formation of free radicals and, further, that these free radicals were of two types—univalent and bivalent. The formation of compounds of the above-mentioned type is then explained by the coupling together of two of the alkyl radicals with one alkylene radical: $R— + R— + RCH{<} \longrightarrow RCHRR$.

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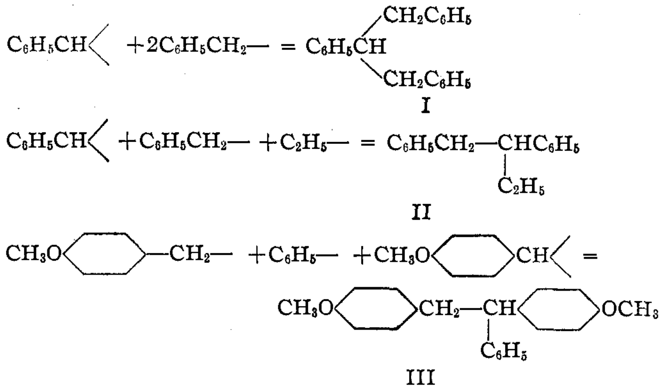
[2] Späth, *Monatsh.*, **34**, 1965 (1913).

In accordance with this scheme the origin of the three compounds reported was represented by the following equations.



(1)

(2)

(3)

I

II

III

In a recent study of the coupling action of methylmagnesium iodide on the benzyl halides the writer[3] failed to obtain the 1,2,3-triphenylpropane reported by Späth and the present investigation was undertaken in order to explain this discrepancy. It is unquestionably due to differences in experimental procedure. A comparison of the two sets of experiments showed that, whereas the writer always used a considerable excess of the Grignard reagent, Späth employed the amounts of the starting materials, magnesium, alkyl halide and benzyl halide required by calculation from the equation. Thus in the case of methylmagnesium iodide and benzyl chloride he used a solution of the former prepared from 4.9 g. (0.2 gram atom) of magnesium and 29 g. (0.2 mole) of methyl iodide. To this solution was added 25.1 g. (0.2 mole) of benzyl chloride.

It is very doubtful if 0.2 mole of active methylmagnesium iodide was actually present in the reaction mixture. Although Houben and Bödler[4] report a yield of 99.83% of this reagent, the experience of the writer has been that unless very special precautions are taken, the yield of active reagent is not more than 90% and is more often about 80% of that calculated. It seems very probable, then, that in the procedure of Späth there was an excess of benzyl chloride.

The presence of unchanged benzyl chloride among the reaction products suggests the possibility that the formation of the supposititious 1,2,3-triphenylpropane was due not to any action of the Grignard reagent but to a reaction between the unchanged benzyl chloride and the coupling product, dibenzyl, which might have taken place during the distillation used in separating the products.

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[3] Fuson, This Journal, **48**, 2681 (1926).

[4] Houben and Bödler, "Die Methoden der organischen Chemie," Georg Thieme, Leipzig, **1924**, vol. 4, p. 725.

p-Benzyldibenzyl and 1,2,3-Triphenylpropane

This surmise has been found to be correct. When dibenzyl is heated alone with benzyl chloride, hydrogen chloride is given off and an oil is obtained having all of the properties given by Späth and others[5] for 1,2,3-triphenylpropane. The product boiled at 225–230° (10 mm.). The reaction was found to be catalyzed by a small amount of zinc dust. Under these conditions, approximately 50% yields are obtained and the reaction is rapid. It is important to note, however, that the catalyst is not essential—without it the reaction time is much longer and the yield lower but the product is the same. The catalytic effect of zinc on the reaction suggested at once the possibility that the reaction involved the replacement of a nuclear hydrogen rather than one attached to the side chain. Zinc dust has long been known to catalyze reactions of this type.[6] The product in this case would be benzyldibenzyl, *ortho* or *para* or more probably a mixture of the two. $C_6H_5CH_2CH_2C_6H_5 + ClCH_2C_6H_5 = C_6H_5CH_2CH_2C_6H_4CH_2C_6H_5 + HCl$.

Parallel experiments with diphenylmethane and benzyl chloride support this point of view. By operating under conditions similar to those used in the case of dibenzyl it was found that diphenylmethane reacted with benzyl chloride to give a mixture of the *o*- and *p*-dibenzylbenzenes. The compounds are known[7] and were further checked by oxidation to dibenzoylbenzenes.

As a further step in the identification of this compound, assumed by Späth to be 1,2,3-triphenylpropane, the real 1,2,3-triphenylpropane was synthesized by the reduction of phenyldibenzyl carbinol with red phosphorus and hydriodic acid. The product was an oil boiling at 179–181° (2 mm.) or 225–230° (10 mm.). Its analysis considered in connection with the method of synthesis showed it to be 1,2,3-triphenylpropane. As was expected, this compound was different from the oil obtained from dibenzyl. Although the two substances have the same boiling point, the same composition and the same molecular weight they differ in density, refractive index and viscosity. The accompanying table shows the actual values.

	n_D^{20}	d_4^{18}	B. p. (10 mm.), °C.
1,2,3-Triphenylpropane	1.6042	1.0482	225–230
p-Benzyldibenzyl	1.5929	1.0394	225–230

Although the viscosities were not measured it was at once apparent that they differed widely—so much in fact that this alone was sufficient to show that the two liquids cannot be the same.

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[5] Claus and Mercklin, *Ber.*, **18**, 2935 (1885). Cohn, *Chem. Centr.*, **69**, II, 284 (1898).

[6] Zincke, *Ann.*, **159**, 374 (1871); **161**, 93 (1872); *Ber.*, **6**, 137 (1873); **9**, 1761 (1876). For a good discussion of the Zincke reaction see Meyer and Jacobson, "Lehrbuch der organischen Chemie," Veit and Co., Leipzig, **1903**, **2**^{2}, p. 57.

[7] Zincke, *Ber.*, **9**, 31 (1876).

The oil obtained by Späth is, therefore, not 1,2,3-triphenylpropane. That it is a nuclear substitution product, namely, a benzyldibenzyl, was finally proved conclusively by oxidation. When oxidized by chromic acid in glacial acetic acid it gave *p*-benzoylbenzoic acid. No evidence of the formation of *o*-benzoylbenzoic acid was obtained but the oxidation was not a clean reaction and the yield of *p*-benzoylbenzoic acid was far from that calculated so that a considerable amount of the *ortho* compound may have been present and yet have escaped detection. It is to be remembered also that the material was obtained by a series of fractional distillations and it is more than likely that any *ortho* isomer which may have been formed in the reaction was removed by this treatment. The oil has been treated, accordingly, as though it were pure *p*-benzyldibenzyl although the experimental evidence does not preclude the presence of some of the *ortho* isomer as a contaminant. Moreover, this possibility has no important connection with the argument with which this paper is concerned.

p-Benzyl-*n*-propylbenzene

In analogy with the foregoing results the compound obtained by treating benzyl chloride with ethylmagnesium bromide and identified by Späth as α-ethyl-α,β-diphenylethane (II) is to be accounted for by a reaction between an excess of benzyl chloride and its ethylation product, *n*-propylbenzene. This compound ought to be a benzyl-*n*-propylbenzene (IV)—*para*, *ortho* or a mixture of the two: $C_6H_5CH_2Cl + C_6H_5CH_2CH_2CH_3 = C_6H_5CH_2C_6H_4CH_2CH_2CH_3$ (IV) + HCl.

Experiment has verified this prediction. Benzyl chloride and *n*-propylbenzene when heated at 150° with a small amount of zinc dust react vigorously with the evolution of hydrogen chloride and the formation of benzyl *n*-propylbenzene. The identity of this compound was established by analysis and by oxidation. On oxidation with chromic acid in glacial acetic acid it yields *p*-benzoylbenzoic acid. Here, again, as in the case previously discussed of *p*-benzyldibenzyl, no evidence was obtained of the presence of the *ortho* isomer but the yield of the oxidation product was far from quantitative and it is possible that some of the *ortho* compound may have been present and escaped detection. Since this question does not materially enter into the problem in hand it was not further investigated.

p-Benzyl-*n*-propylbenzene has almost the same boiling point as α-ethyl-α,β-diphenylethane but differs from it in refractive index and density. The comparative figures are given below.

α-Ethyl-α,β-diphenylethane: $n_D^{20} = 1.587$; $d_0^{18} = 1.0092$.[8] *p*-Benzyl-*n*-propylbenzene: $n_D^{18} = 1.5552$; $d_4^{18} = 0.9737$.

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[8] Sabatier and Murat, *Compt. rend.*, **156,** 1430 (1913).

The difference in the boiling points is hardly significant but the densities and refractive indices show that the two liquids are different.

Experimental Part

1,2,3-Triphenylpropane.—This hydrocarbon was prepared by reducing phenyldibenzylcarbinol obtained from benzylmagnesium chloride and ethyl benzoate by the method of Klages and Heilmann.[9]

A mixture of 14.4 g. of the carbinol, 28.5 g. of 45% hydriodic acid, 1.6 g. of red phosphorus and 75 cc. of glacial acetic acid was refluxed for 20 hours. The excess of phosphorus was then removed by filtration and the filtrate poured onto ice. The product, which appeared as an oil, was separated, dried and distilled. It boiled at 179–181° (2 mm.) or 225–230° (10 mm.); yield, 4.4 g., or 32%; $d_4^{18} = 1.0482$; $n_D^{23} = 1.6042$.

Anal. Calcd. for $C_{21}H_{20}$: C, 92.6; H, 7.4. Found: C, 92.5; H, 7.8.

The compound was a viscous, very slightly yellow oil. It did not reduce permanganate in cold acetone solution.

p-Benzyldibenzyl.—This compound was prepared by the interaction of benzyl chloride and dibenzyl by the elimination of hydrogen chloride. The reaction proceeds slowly without a catalyst (see below) and is rapid in the presence of a small quantity of zinc dust. The following procedure, which is essentially the method of Zincke,[6] was found to be the most satisfactory.

A mixture of 40 g. (0.22 mole) of dibenzyl and 28 g. (0.22 mole) of benzyl chloride was heated to about 150° in a brominating flask. The addition of a small amount of zinc dust initiated a vigorous reaction; hydrogen chloride was evolved and the mixture continued to boil spontaneously for about 15 minutes. Heating was then resumed and continued until the evolution of gas had practically ceased. This required about an hour.

The mixture was distilled directly first with a water pump and then with an oil pump. In this way 18 g. of dibenzyl was recovered and a yield of 17 g. of benzyldibenzyl, b. p. 213–216° (5 mm.) or 225–230° (10 mm.), was obtained. The yield based on the amount of dibenzyl actually used up in the reaction is 52%; $d_4^{18} = 1.0394$; $n_D^{23} = 1.5929$.

Anal. Calcd. for $C_{21}H_{20}$: C, 92.6; H, 7.4. Found: C, 92.9; H, 7.2.

Mol. wt. Calcd. for $C_{21}H_{20}$: mol. wt., 272. Found: 286.

The compound is a colorless, mobile liquid when pure but has a yellow color and a slight fluorescence in the impure form obtained by the first distillation. It is sharply distinguished from 1,2,3-triphenylpropane by its low viscosity. It does not reduce permanganate in cold acetone solution.

From theoretical considerations previously advanced, the following preparation involving the use of no catalyst is important. Twelve g. (0.09 mole) of benzyl chloride was added dropwise to 19 g. (0.10 mole) of boiling dibenzyl. As soon as addition was begun, hydrogen chloride began to be evolved. The addition was completed in four hours and the reaction mixture was subsequently heated for two hours. Fractional distillation gave 10 g. of unchanged dibenzyl and 4.0 g. of benzyldibenzyl identical with that obtained when zinc was used as a catalyst. The yield in this case is 30% of the amount obtainable from 9 g. of dibenzyl, the quantity actually used up in the reaction. In this as in the first procedure a large, highly fluorescent, viscous residue was obtained.

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[9] Klages and Heilmann, *Ber.*, **37**, 1456 (1904).

Oxidation.—One g. of benzyldibenzyl was treated with a mixture of 4 g. of chromic anhydride and 50 cc. of glacial acetic acid. The crude acid so obtained melted at 180–188°. It was recrystallized from hot water in fine, silky needles melting at 191–193°.

In order to make certain the identity of the oxidation product, *p*-benzoylbenzoic acid, it was esterified. Treatment with methyl alcohol and concd. sulfuric acid gave an ester which, after one recrystallization from methyl alcohol, melted sharply at 107°. This ester is known, having been prepared by Plaskuda[10] who gives its melting point as 107°.

***p*-Benzyl-*n*-propylbenzene.**—A mixture of 16 g. (0.13 mole) of *n*-propylbenzene and 20 g. (0.16 mole) of benzyl chloride was heated to about 150° and a trace of zinc dust was dropped in. A vigorous reaction took place accompanied by the evolution of hydrogen chloride. The heating was continued for 45 minutes, at the end of which time the evolution of gas had practically ceased. The mixture was distilled under diminished pressure. A few cubic centimeters of unchanged material came over, then a fraction of 7 g. boiling at 140–180° (6 mm.) was collected. This, on redistillation, came over almost completely at 152–155° (10 mm.). The *p*-benzyl-*n*-propylbenzene so obtained is a colorless, mobile liquid.

Anal. Calcd. for $C_{16}H_{18}$: C, 91.4; H, 8.6. Found: C, 91.0; H, 8.5. $d_4^{18} = 0.9739$. $n_D^{20} = 1.5552$.

Oxidation.—One g. of *p*-benzyl-*n*-propylbenzene was refluxed for three hours in a mixture of 4 g. of chromic anhydride and 50 cc. of glacial acetic acid. The oxidation product was isolated in the manner described above for the case of *p*-benzyldibenzyl. There resulted 0.4 g. of *p*-benzoylbenzoic acid; m. p., 192–194°; yield, 40%. The identity of this compound was established by a mixed-melting-point determination with a known sample of the acid.

Summary

The supposititious 1,2,3-triphenylpropane obtained by Späth from the action of various Grignard reagents on benzyl halides has been shown to be in reality *p*-benzyldibenzyl. It is formed not by any action of the Grignard reagent but by the elimination of hydrogen halide between an excess of benzyl halide and the coupling product, dibenzyl: $C_6H_5CH_2X + C_6H_5CH_2CH_2C_6H_5 = C_6H_5CH_2C_6H_4CH_2CH_2C_6H_5 + HX$.

The compound obtained by Späth by the interaction of ethylmagnesium bromide and benzyl chloride and supposed to be α-ethyl-α,β-diphenylethane has been shown to be *p*-benzyl-*n*-propylbenzene.

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[10] Plaskuda, *Ber.*, **7**, 988 (1874).