

ml. of freshly prepared sodium hypochlorite solution.<sup>18</sup> Stirring was continued for 15 minutes at room temperature and then at reflux temperature for 30 minutes. Acetone was added to destroy excess hypochlorite and the cooled solution acidified with dilute sulfuric acid. The crude product was isolated by ether extraction followed by sodium bicarbonate extraction and acidification. One recrystallization from 7 ml. of dioxane, trituration with two 7-ml. portions of chloroform, and a final recrystallization from 15 ml. of water gave 150 mg. of white crystals melting at 274–276°. By reworking the filtrates and washings, an additional 30 mg. of product (total yield 180 mg. (24.8%)) and 130 mg. of an impure chloro-compound, m.p. 190–230°, were obtained. A sublimed sample melted at 274–276°, corresponding to the literature value,<sup>19</sup> and showed no depression when mixed with an authentic sample prepared by partial demethylation of isohemipinic acid.<sup>13</sup> *Anal.* Calcd. for C<sub>9</sub>H<sub>8</sub>O<sub>6</sub>: C, 50.95; H, 3.80; OCH<sub>3</sub>, 14.61. Found: C, 51.0; H, 4.15; OCH<sub>3</sub>, 14.9.

**Vanillin-5-carboxylic Acid (VI).**—To a stirred solution of 2.4 g. of VII in 40 ml. of dioxane and 40 ml. of 10% sodium hydroxide was added, over one minute, 50 ml. of sodium hypochlorite solution.<sup>18</sup> After 20 minutes at room temperature and 30 minutes at reflux temperature, acetone was

added to destroy excess hypochlorite and the reaction mixture cooled and acidified. The product was removed from an ether extract with 10% sodium bicarbonate solution. The bicarbonate layer, freed of dioxane and acetone by ether extraction, was acidified with dilute sulfuric acid and extracted with ether. A sodium bisulfite extract of this ether layer was filtered, acidified, aerated and then extracted with ether. After drying the extract, the ether was removed. The crude product was vacuum-sublimed twice and then recrystallized from water. The pure product, 30 mg. (2.1%), melted at 253–255°. A mixed melting point with an authentic sample of vanillin-5-carboxylic acid showed no depression.

### Summary

5-Acetylvanillin (2-hydroxy-3-methoxy-5-formylacetophenone), which has been proposed to be the monomeric unit in the formation of a lignin-like polymer, has been prepared by a five-step synthesis from *o*-vanillin.

The structure of this compound was established by converting it to 4-hydroxy-5-methoxisophthalic acid and to vanillin-5-carboxylic acid. Mixed melting points of these products with authentic samples showed no depression.

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(18) Chlorine was passed into 20 ml. of 20% sodium hydroxide to neutrality. The solution was stabilized with an additional 5 ml. of base.

(19) Freudenberg and Klinck, *Ber.*, **73B**, 1369 (1940).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF DELAWARE]

## Acid-catalyzed Rearrangement of Some Aromatic Ketones<sup>1</sup>

BY WILLIAM A. MOSHER AND MELVIN L. HUBER<sup>2</sup>

In the course of a study of the reactions of Grignard reagents with  $\beta$ -benzopinacolone, we had occasion to reinvestigate the results in this connection reported by Schmidlin and Wohl.<sup>3</sup> These workers studied the forced reaction of phenylmagnesium iodide with  $\beta$ -benzopinacolone and reported "dehydropentaphenylethanol" as one of the products and described its isomerization with sulfuric acid to "isodehydropentaphenylethanol." However, the structures of these two compounds were not established.

When "dehydropentaphenylethanol" was oxidized with chromic anhydride in aqueous acetic acid, triphenylcarbinol and *o*-phenylbenzoic acid were obtained.<sup>4</sup> When heated with potassium hydroxide in alcohol, triphenylmethane and *o*-phenylbenzoic acid were formed. This latter method of cleavage has been used extensively in the determination of the structures of pinacolones in the aromatic series.<sup>5</sup> A new pinacolone which was identical with the product of the forced Grignard addition was synthesized by coupling triphenylmethylsodium with *o*-phenylbenzoyl chlo-

ride. "Dehydropentaphenylethanol" is, therefore, *o*-biphenyl triphenylmethyl ketone (I) which is formed by 1,4-addition of the Grignard reagent into the phenyl ring.

The infrared absorption spectra of "dehydropentaphenylethanol" (I) showed strong carbonyl absorption but was negative for the hydroxyl band; "isodehydropentaphenylethanol," on the other hand, was positive for hydroxyl but showed no carbonyl absorption band. Its structure was established by cleavage with potassium hydroxide to yield *o*-( $\alpha,\alpha$ -diphenyl-*o*-tolyl)-benzophenone (III) and by oxidation with chromic acid to give the "keto-carbinol" (IV) described by Sergeev,<sup>6a,b</sup> The structure of the new ketone (III) was established by its cleavage into *o*-( $\alpha,\alpha$ -diphenyl-*o*-tolyl)-benzoic acid on fusion with potassium hydroxide and by its synthesis from the methyl ester of *o*-( $\alpha,\alpha$ -diphenyl-*o*-tolyl)-benzoic acid with one mole of phenylmagnesium bromide and also by its conversion with phenyl Grignard to the tertiary alcohol, *o*-(*o*-benzohydrylphenyl)-triphenylcarbinol, previously prepared.<sup>6b</sup> "Isodehydropentaphenylethanol" is therefore 9,10,10-triphenyl-9,10-dihydro-9-phenanthrol (II). This structure was confirmed by synthesis involving the reaction of phenyllithium on 10,10-diphenyl-9-phenanthrone (V). These facts are summarized in Fig. 1.

The rearrangement of *o*-biphenyl triphenylmethyl ketone was so unusual that the same reaction was employed using the related  $\alpha$ -naphthyl triphenylmethyl ketone. In this case rearrangement was somewhat slower but the principal prod-

(1) Presented before the Division of Organic Chemistry, American Chemical Society, Philadelphia, April, 1950. This manuscript taken from the Ph.D. dissertation of M. L. Huber, School of Graduate Studies, University of Delaware, 1950.

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(3) Schmidlin and Wohl, *Ber.*, **43**, 1145 (1910).

(4) Schmidlin and Wohl<sup>3</sup> reported the formation of  $\beta$ -benzopinacolone when "dehydropentaphenylethanol" was oxidized with chromic anhydride in acetic acid solution. We have not been able to duplicate this observation although our "dehydropentaphenylethanol" has properties identical with those reported by them and it is converted to "isodehydropentaphenylethanol" identical in properties with theirs.

(5) Cf. W. E. Bachmann and J. W. Ferguson, *THIS JOURNAL*, **56**, 2081 (1934).

(6) (a) Chichibabin and Sergeev, *Ber.*, **59**, 657 (1926); (b) Sergeev, *J. Russ. Phys.-Chem. Soc.*, **61**, 1421 (1929).

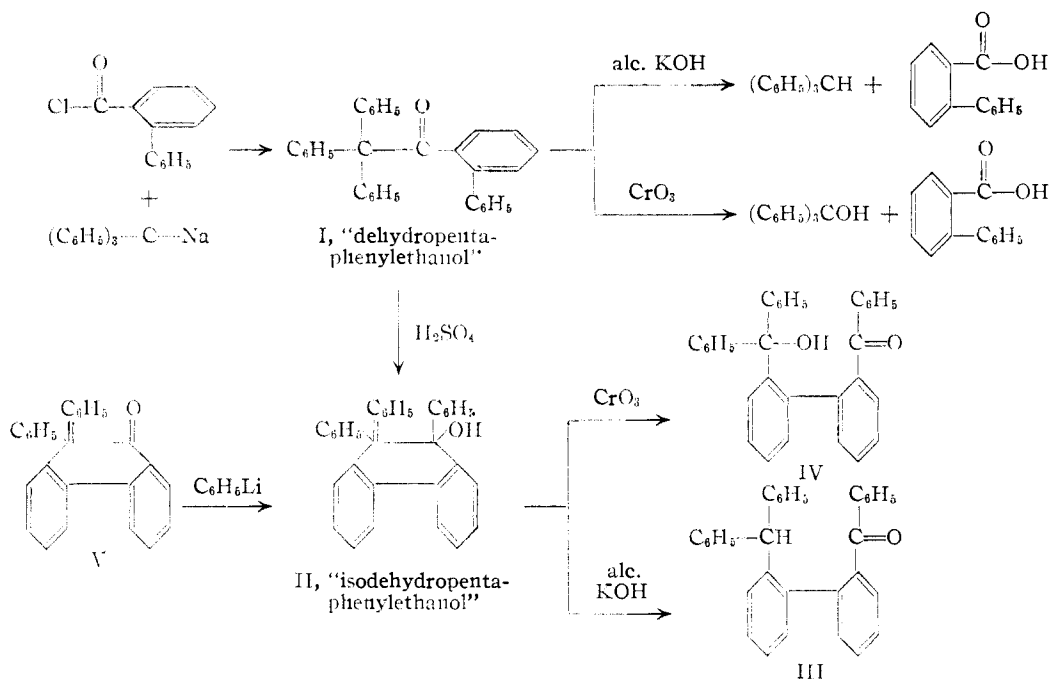


Fig. 1.

uct was 1,2,2-triphenyl-1-acenaphthenol. This compound had been previously prepared by Wittig and Petri.<sup>7</sup> The pinacolone used by us, however, is a new substance; it was prepared by the action of triphenylmethylsodium on  $\alpha$ -naphthoyl chloride and its structure was confirmed by its oxidation to triphenylcarbinol and *o*-phthalic acid and its cleavage with alkali into triphenylmethane and  $\alpha$ -naphthoic acid.

The probable mechanism for the acid-catalyzed rearrangement of the ketone (I) is summarized in Fig. 2. In some respects the process parallels

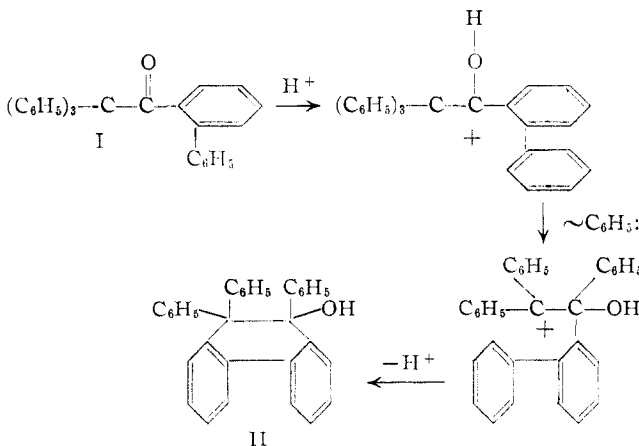


Fig. 2.

the ionic mechanism already suggested for the cyclization of ketones to form anthracene derivatives<sup>8,9</sup> and phenanthrene derivatives<sup>10</sup> and serves to add very convincing support for these proposals. This cyclization differs in that the elements of

water cannot be lost to yield a phenanthrene derivative; aromatization by loss of phenol has not been found to occur.<sup>11</sup> In addition, the fact that a phenyl group migrates during the cyclization process is unusual, but this can be readily explained by the formation of the conjugate acid of the ketone followed by migration of a phenyl group from an adjacent carbon to the positive center. This rearrangement should not be considered as an example of the retro-pinacolone rearrangement<sup>12</sup> in which a positive center is formed on carbon by loss of hydroxyl during a dehydration process. Here we are confronted with the formation of both a positive center on carbon and a new hydroxyl group. The cyclization is completed by an intramolecular condensation, of the Friedel-Crafts type, when the carbonium ion attacks the ortho position of the adjacent ring. Bradsher<sup>11</sup> considered the possibility of a similar migration in a positive ion formed from an epoxide; in that case, however, the shift was away from the hydroxyl bearing carbon rather than to it.

This reaction offers a new synthesis of triaryldihydrophenanthrols and it may be a convenient method for preparing certain highly hindered aromatic alcohols where steric considerations make other approaches impossible or difficult. The extension of this general process is now under consideration with other systems.

The oxidation of 9,10,10-triphenyl-9,10-dihydro-9-phenanthrol justifies further discussion because of its structural relationship to pentaphenylethanol; the only difference lies in the fact that ring closure has taken place between ortho positions of phenyl groups attached to adjacent carbon

(7) Wittig and Petri, *Ber.*, **68**, 924 (1935).(8) Berliner, *THIS JOURNAL*, **64**, 2894 (1942).(9) Bradsher and Smith, *ibid.*, **65**, 854 (1943).(10) Bradsher and Wissow, *ibid.*, **68**, 1094 (1946).(11) Cf. Bradsher, Rapaport and Anderson, *ibid.*, **68**, 2152 (1946).(12) Bachmann, *ibid.*, **55**, 3857 (1933).

atoms. Oxidation of triphenylcarbinol with chromic anhydride in acetic acid yields benzophenone in good yield and small amounts of material suspected of being derived from the oxidation of phenol.<sup>13</sup> Our interest in the related pentaphenylethanol, which Schmidlin and Wohl attempted to prepare,<sup>3</sup> lay primarily in the fact that on oxidation with chromate it might yield benzophenone and triphenylcarbinol, both of which are reasonably resistant to further attack. Fortunately, the phenylated phenanthrol is better suited for oxidative study because there is no apparent spontaneous dissociation and functional groups are retained in the same molecule. Applying concepts previously advanced from this Laboratory<sup>14</sup> the formation of the keto-carbinol was predicted. The proposed mechanism is indicated in Fig. 3.

**Acknowledgment.**—We are grateful to the Research Corporation for an F. G. Cottrell Grant which made this work possible.

### Experimental<sup>15</sup>

***o*-Biphenyl Triphenylmethyl Ketone (I).**— $\beta$ -Benzopinacolone was treated with an excess of phenylmagnesium iodide in a manner similar to that described by Schmidlin and Wohl.<sup>3</sup> Unless special precautions were taken, this aromatic ketone (I) ("dehydropentaphenylethanol") was the main product isolated. It was recrystallized from ether, benzene or benzene-alcohol (1:1), m.p. 189–190°.

*Anal.* Calcd. for C<sub>32</sub>H<sub>24</sub>O: C, 90.53; H, 5.70. Found: C, 90.30; H, 5.30.

**Proof of Structure of *o*-Biphenyl Triphenylmethyl Ketone (I).**—One-half gram of I, obtained from the Grignard addition, was refluxed for 48 hours with about 55 cc. of a 15% alcoholic potassium hydroxide solution. After filtration, dilution, and cooling, 0.25 g. of triphenylmethane was obtained; m.p. and mixed m.p. 90–91°. After acidification of the filtrate, 0.1 g. of *o*-phenylbenzoic acid was isolated; m.p. and mixed m.p. 110–112°.

To 1.5 g. of I dissolved in 100 cc. of acetic acid at 60° there was added during 1 hour a solution of 3 g. of chromic anhydride in 35 cc. of acetic acid containing a few drops of water. After 2 hours additional heating at 60° the mixture was diluted. Recrystallization of the solid formed yielded 0.5 g. of triphenylcarbinol, m.p. and mixed m.p. 160–162°. Further treatment of the filtrate produced 0.1 g. of *o*-phenylbenzoic acid, m.p. and mixed m.p. 110–112°. Calcd.: neut. equiv., 198. Found: neut. equiv., 202.

**Synthesis of *o*-Biphenyl Triphenylmethyl Ketone (I).**—Triphenylmethyl sodium was obtained by shaking 45 g. of triphenylmethyl chloride for 8.5 hours in a sealed container with 3% sodium amalgam.<sup>16</sup> The ether solution of the organometallic compound was transferred to a 500-cc., three-necked flask by a slight positive nitrogen pressure and an inert atmosphere was maintained during the coupling reaction. About 28 g. of crude *o*-phenylbenzoyl chloride in ether was added dropwise with stirring so as to maintain a gentle reflux and the mixture became green-brown in color. After stirring, for one-half hour longer, it was poured into ice-water and the precipitate was filtered quickly in several passes. The gray precipitate was treated with aqua regia and then filtered after dilution. Recrystallization from benzene or benzene-alcohol (1:1) yielded the product m.p. 189–190°. Additional ketone was isolated from the ether filtrate after passing air through the mixture and filtering

(13) W. A. Mosher, H. A. Neidig and M. L. Huber, paper presented before Division of Organic Chemistry, American Chemical Society, New York, September, 1947.

(14) Mosher and Whitmore, *THIS JOURNAL*, **70**, 2544 (1948); Mosher and Langerak, *ibid.*, **71**, 286 (1949); Mosher and Neidig, *ibid.*, **73**, 4452 (1950).

(15) All melting points were observed between cover glasses using a Fisher-John melting point apparatus.

(16) "Organic Syntheses," Coll. Vol. II, John Wiley & Sons, Inc., New York, N. Y., p. 607.

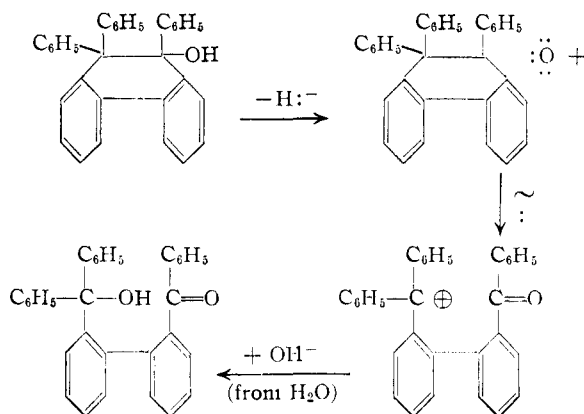


Fig. 3.

off the triphenylmethyl peroxide; total yield 30 g. (50%). A mixture with "dehydropentaphenylethanol" showed no depression on melting and the ketone showed the characteristic green color with sulfuric acid.<sup>3</sup> This color is produced by the rearranged product (see below).

*Anal.* Calcd. for C<sub>32</sub>H<sub>24</sub>O: C, 90.53; H, 5.70. Found: C, 90.47; H, 5.50.

**Rearrangement of *o*-Biphenyl Triphenylmethyl Ketone (I).**—The general procedure described by Schmidlin and Wohl<sup>3</sup> was followed, but it was found that the time of reaction may be reduced from 6 days to 3 days (and perhaps less) with better yields and a cleaner product. The green reaction solution was hydrolyzed with ice and extracted with additional benzene. The solvent layer was washed and allowed to evaporate. The brown color was removed from the residue with minimum amounts of benzene and the product was recrystallized from benzene or benzene-alcohol (1:1), m.p. 231.5–232.5°. The product, 9,10,10-triphenyl-9,10-dihydro-9-phenanthrol (II), was formed in 57% yield. This carbinol dissolved in sulfuric acid with the formation of a dark green solution from which the original material was regenerated on dilution.

*Anal.* Calcd. for C<sub>32</sub>H<sub>24</sub>O: C, 90.53; H, 5.70. Found: C, 90.25; H, 5.41.

**Synthesis of 9,10,10-Triphenyl-9,10-dihydro-9-phenanthrol (II).**—Twelve and one-half grams of the ketone in 75 cc. of dry ether was treated in an atmosphere of nitrogen with a filtered solution of phenyllithium made from 10 cc. of bromobenzene. In the single run made, the ether evaporated accidentally during the subsequent reflux period of 2 hours and a white residue resulted. Addition of ether and hydrolysis gave a light orange solvent layer in which the insoluble product appeared. The solid was recrystallized from benzene-alcohol (1:1); yield 8 g. (50%), m.p. 231.5–232.5°. A mixture with the rearranged product (above) gave no depression on melting.

*Anal.* Calcd. for C<sub>32</sub>H<sub>24</sub>O: C, 90.53; H, 5.70. Found: C, 90.62; H, 5.52.

**Proof of Structure of 9,10,10-Triphenyl-9,10-dihydro-9-phenanthrol (II).**—The oxidation of II with chromic anhydride gave the ketone-carbinol, IV (see below).

Three and two-tenths grams of the rearranged product (II) was refluxed for 15 hours with about 190 cc. of a 15% alcoholic potassium hydroxide solution. After several hours, crystals began to form on the walls of the flask. After cooling and filtering, the product was recrystallized from benzene or benzene-alcohol and a high yield of *o*-( $\alpha,\alpha$ -diphenyl-*o*-tolyl)-benzophenone (III) was obtained, m.p. 178–179°.

*Anal.* Calcd. for C<sub>22</sub>H<sub>24</sub>O: C, 90.53; H, 5.70. Found: C, 90.25; H, 5.41.

**Proof of Structure of *o*-( $\alpha,\alpha$ -Diphenyl-*o*-tolyl)-benzophenone (III).**—One-half gram of III (above) was fused with potassium hydroxide. After cooling, solution, filtration and acidification, the product was found to be *o*-( $\alpha,\alpha$ -diphenyl-*o*-tolyl)-benzoic acid. After recrystallization from alcohol it melted at 177–179° and there was no depression on melting a mixture with an authentic specimen obtained by a similar fusion of V.

Two-tenths gram of III was treated with a Grignard solution made from about 2 g. of bromobenzene. Hydrolysis

of the purple solution gave a product, insoluble in the ether layer, which was recrystallized from carbon tetrachloride-alcohol, m.p. 238–240°. This is the tertiary alcohol, *o*-(*o*-benzohydroxyphenyl)-triphenylcarbinol reported by Sergeev.<sup>6b</sup> A true sample made from the reaction of phenyl Grignard on the methyl ester of *o*-( $\alpha,\alpha$ -diphenyl-*o*-tolyl)-benzoic acid gave no depression when mixed with III and melted.

This ketone (III) was synthesized by the cautious addition of 1 mole of phenylmagnesium bromide to the methyl ester of *o*-( $\alpha,\alpha$ -diphenyl-*o*-tolyl)-benzoic acid, but the product was difficult to purify and the melting point was several degrees low. Further treatment with more of the Grignard solution gave the tertiary alcohol described above.

**Synthesis of  $\alpha$ -Naphthyl Triphenylmethyl Ketone.**—This pinacolone was made from triphenylmethylsodium and  $\alpha$ -naphthoyl chloride in a manner analogous to that described above for I. The ether solution after hydrolysis was oxidized with air and allowed to evaporate. The oil was taken up in ether, filtered to remove the triphenylmethyl peroxide, washed with 10% sodium hydroxide, and evaporated. Treatment of the residual oil with a mixture of ether, petroleum ether (65–110°) and benzene produced a yellow solid from which the color was removed by recrystallizations from acetic acid. In concentrated sulfuric acid, it gradually forms a dark green color; m.p. 157–158°.

*Anal.* Calcd. for  $C_{30}H_{22}O$ : C, 90.41; H, 5.57. Found: C, 90.38; H, 5.40.

**Proof of Structure of  $\alpha$ -Naphthyl Triphenylmethyl Ketone.**—Three-fourths gram of the ketone refluxed for 44 hours with about 55 cc. of a 15% alcoholic potassium hydroxide solution gave a mixture from which there was isolated 0.4 g. of triphenylmethane (m.p. and mixed m.p. 90–92°) and 0.28 g. of  $\alpha$ -naphthoic acid (m.p. and mixed m.p. 159–161°).

One gram of ketone dissolved in 100 cc. of acetic acid was oxidized at 60° with 3.25 g. of chromic anhydride in 30 cc. of acetic acid containing several drops of water. The oxidant was added during 1 hour and the temperature was maintained for 4 hours longer. After dilution and extraction with benzene-ether, the solvent layer was extracted with 10% sodium hydroxide. Evaporation of the solvent gave triphenylcarbinol and treatment of the alkaline extract yielded an acidic material, melting near 200°, which gave a strong fluorescein test. The latter was probably *o*-phthalic acid from the oxidation of the  $\alpha$ -naphthoic acid first formed.

**Rearrangement of  $\alpha$ -Naphthyl Triphenylmethyl Ketone.**—Four and eight-tenths grams of the ketone was dissolved in 175 cc. of dry benzene and 200 cc. of concentrated sulfuric acid and the mixture was shaken mechanically for 11 days. After hydrolysis of the green solution with ice, more benzene was added and the solvent layer was washed and evaporated. The residual oil was treated with petroleum ether (30–65°) and benzene was added dropwise until a solid formed. This material was recrystallized several times from benzene-petroleum ether (65–110°) (1:2), m.p. 169–170°. The product was 1,2,2-triphenyl-1-acenaphthenol which has been characterized previously.<sup>7</sup> Treatment of the isomerization product with acidic methanol gave a product melting at 174–175° corresponding to the methyl ether of this carbinol.

**Oxidation of 9,10,10-Triphenyl-9,10-dihydro-9-phenanthrol (II).**—Two grams of the carbinol, dissolved in 125 cc.

of warm benzene, and 5.1 g. of chromic anhydride, dissolved in 5 cc. of water and 50 cc. of acetic acid, was added dropwise from separate funnels into 200 cc. of acetic acid which was stirred and heated on a steam-bath. (Preliminary studies indicate the quantity of oxidant is important in the formation of the product described.) After the addition period of three-fourths of an hour, heating was continued for a similar period and after cooling slightly, the mixture was poured into about 500 cc. of water. The solvent layer, plus additional extractions, was washed in two portions with 180 cc. of a 10% sodium carbonate solution, once with water, and then evaporated. The red residual oil was rubbed with about 15 cc. of acetic acid and filtered after one-half hour. Recrystallization of the insoluble material from acetic acid and several times from alcohol gave *o*-(*o*-benzoylphenyl)-triphenylcarbinol (IV), m.p. 191–192°. The melting point remained unchanged when this was mixed with the "keto-carbinol" described by Sergeev.<sup>6a,b</sup>

*Anal.* Calcd. for  $C_{32}H_{24}O_2$ : C, 87.24; H, 5.49. Found: C, 87.01; H, 5.98.

**Infrared Spectral Analysis.**—Spectra were obtained on a Baird double beam infrared recording spectrophotometer from solid samples in the form of a "Nujol" mull.

The spectrum of the product (IV) from the oxidation of II showed strong hydroxyl absorption at 2.9–3.0  $\mu$  and strong ketone absorption at 6.1  $\mu$  and, except for the hydroxyl band, the curve resembles closely the spectrum of III. This confirms the presence of two functional groups in the solid oxidation product (IV).

The spectrum of I indicated no hydroxyl absorption but a strong ketone peak appeared at 5.9–6.0  $\mu$ . The curve from II showed a definite hydroxyl band at 2.8–2.9  $\mu$  but ketone absorption was absent.

### Summary

1. The "dehydropentaphenylethanol" described by Schmidlin and Wohl from the reaction of  $\beta$ -benzopinacolone and phenylmagnesium iodide is *o*-biphenyl triphenylmethyl ketone formed by a 1,4-addition of the Grignard reagent.

2. The "isodehydropentaphenylethanol" formed by the action of sulfuric acid on "dehydropentaphenylethanol" is 9,10,10-triphenyl-9,10-dihydro-9-phenanthrol formed by an unusual acid-catalyzed rearrangement. A mechanism is proposed for this isomerization.

3. On treatment with sulfuric acid,  $\alpha$ -naphthyl triphenylmethyl ketone rearranges in like manner to 1,2,2-triphenyl-1-acenaphthenol.

4. This rearrangement offers a new mode of synthesis of highly hindered condensed ring compounds.

5. The oxidation of 9,10,10-triphenyl-9,10-dihydro-9-phenanthrol yields on chromate oxidation a keto-carbinol in harmony with the electronically deficient oxygen intermediate hypothesis.

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