2. The preparation of the acid was brought about by two operations: (1) the condensation of molecules of proper constitution in the molecular proportions to synthesize the desired nitril or ester; (2) the hydrolysis of the nitril or ester.

3. Two methods were used to bring about the condensation: (1) aldehydes of the fatty acid series were converted to the cyanohydrines and condensed with benzyl cyanide by means of sodium ethoxide or sodium methoxide; (2) esters of α-bromo fatty acids were condensed with benzyl cyanide by means of sodamide.

4. The complete hydrolysis of the nitrils or esters of *iso*propyl- and *iso*-butyl-phenyl-succinic acid cannot be brought about by the usual acid or alkali methods, but these substances must be heated in a bomb tube at 130–140° for from 24 to 30 hours.   This resistance to hydrolysis is probably due to a steric hindrance effect, to an electrochemical effect of the sub-stituted alkyl group, or to a combination of the two effects.

5. The general properties of each acid vary according to its constitution.

6. A new formula is suggested for the compound formed when sodamide reacts with benzyl cyanide in ether solution.

LINCOLN, NEBRASKA.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN.]

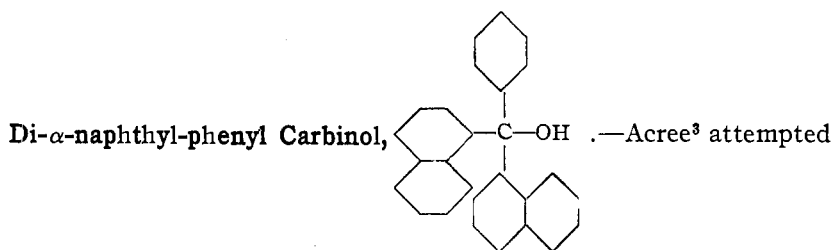# DI-α-NAPHTHYL-PHENYL CARBINOL AND DI-α-NAPHTHYL-PHENYL-METHYL.

BY C. S. SCHOEPFLE.

In a previous paper,[1] it has been shown that the hexa-aryl-ethane, di-α-naphthyl-tetraphenyl-ethane, is dissociated to a very marked extent into the free radical, α-naphthyl-diphenyl-methyl, $R_3C\!-\!CR_3 \rightleftharpoons 2\ R_3C$. This dissociation is influenced by the nature of the solvent, the concentration of the radical in solution, and by the temperature, the latter being the most important factor.   Molecular-weight determinations in various solvents freezing at temperatures from 6° to 80°, showed that at 6° the radical exists as 30% dimolecular and 70% monomolecular, the dissociation increasing until at approximately 62° only the monomolecular form is present in solution.   However, above this temperature the molecular weight continues to decrease, showing that a further dissociation of the monomolecular form must be taking place, the nature of which could not be ascertained.   With the hope of obtaining more information concerning this interesting phenomenon, a study of the free radical di-α-naphthyl-phenyl-methyl was undertaken, since it was known that the naphthyl group exerts a great influence on the extent of the dissociation.[2]

[1] Gomberg and Schoepfle, THIS JOURNAL, 41, 1655 (1919).

[2] Gomberg and Schoepfle, *ibid.*, 39, 1672 (1917).

Di-α-naphthyl-phenyl Carbinol, [structure] .—Acree[3] attempted

to prepare di-α-naphthyl-phenyl carbinol from benzoyl chloride and α-naphthyl-magnesium bromide, but found that only α-naphthyl-phenyl ketone was formed. Elbs[4] obtained the carbinol by heating α-naphthyl-phenyl-β-pinacoline with alcoholic potash, and describes it as a grayish-yellow crystalline crust from ether-alcohol; m. p. 160–170°.

In repeating Acree's experiment, it was found that when benzoyl chloride and α-naphthyl-magnesium bromide are allowed to ·react in ether solution, the impure product which is obtained upon decomposition with water and dilute acid consists mainly of α-naphthyl-phenyl ketone but contains a small amount of di-α-naphthyl-phenyl carbinol which can be isolated only with considerable difficulty. The substitution of ethyl benzoate for benzoyl chloride gives a purer product but, again, the yield of the carbinol is very low, about 10%. When, however, the reaction between ethyl benzoate and α-naphthyl-magnesium bromide is carried out at a higher temperature, 100–110°, then the yield of the carbinol is increased to about 30–35%. The procedure is as follows. The Grignard reagent is prepared in the usual manner from 10 g. of magnesium and 75 g. of α-naphthyl bromide in ether. When the reaction is completed, the ether is distilled under reduced pressure, toluene is added, and the flask is immersed in an oil-bath heated to 110–115°. Twenty-five g. of ethyl benzoate is then added slowly to the boiling solution, and after an additional 10–15 minutes' heating, the flask is cooled and the product decomposed with ice and dil. hydrochloric acid. After evaporation of the solvent, the residue is distilled with steam and taken up in benzene, from which the carbinol is obtained in large, colorless crystals containing 1.5 molecules of benzene of crystallization. Yield, about 25 g.

The carbinol is readily soluble in chloroform, carbon disulfide, carbon tetrachloride, ethyl acetate, acetone and ether, fairly soluble in benzene, less soluble in alcohol and acetic acid, and very slightly soluble in petroleum ether. The melting point of the pure carbinol is 166–167°. With conc. sulfuric acid and with perchloric acid, it gives a deep purple color which, however, is transient and soon disappears.

Calc. for $C_{27}H_{20}O$: C, 89.96; H, 5.60. Found: C, 89.97, 89.76; H, 5.61, 5.53.

[3] Acree, *Ber.*, **37**, 625 (1904).
[4] Elbs. *J. prakt. Chem.*, **35**, 507 (1887).

Additive Compounds with Various Solvents.—The carbinol forms additive compounds with ether, ethyl acetate, acetone, ethyl alcohol, and benzene. The resulting compound in the case of the first 4 solvents consists of one molecule of the carbinol and one molecule of the solvent; for example, $C_{27}H_{20}O.C_2H_5OH$. With benzene, the compound $2C_{27}H_{20}O.3C_6H_6$ is formed. These additive compounds are perfectly stable and at room temperature, do not lose the solvent of crystallization even *in vacuo.* They show melting points ranging from 75–100°, at which temperatures the solvent of crystallization is given off.

With chloroform, carbon disulfide, carbon tetrachloride, acetic acid and petroleum ether, no additive compounds are formed.

Di-α-naphthyl-phenyl-chloromethane and -bromomethane.—Di-α-naphthyl-phenyl-chloromethane was prepared by treating di-α-naphthyl-phenyl carbinol with acetyl chloride. Ten g. of the carbinol $(2C_{27}H_{20}O.3C_6H_6)$ is dissolved in benzene and 10 g. of acetyl chloride added. After standing for a short time, the solution is concentrated under reduced pressure while the temperature of the solution is kept below 50° to prevent decomposition. Upon the addition of petroleum ether, clusters of colorless crystals are obtained in almost quantitative yield. The material used for the preparation of the free radical was always recrystallized from benzene by the addition of petroleum ether to remove any traces of acid. The chloride is not very stable and slowly becomes colored on standing. It melts at 165–167° with decomposition, and loss of hydrogen chloride.

The chloride was also prepared by passing dry hydrogen chloride into a solution of di-α-naphthyl-phenyl carbinol, but a small amount of the chloride-hydrochloride, $C_{27}H_{19}Cl.HCl$, was usually formed. This compound, which has a deep purple color, is unstable and rapidly decomposes to form phenyl-di-α-naphthofluorene. Therefore this method often gives an impure product.

Analysis. Calc. for $C_{27}H_{19}Cl$: Cl, 9.36. Found: 9.21.

If di-α-naphthyl-phenyl carbinol is treated with acetyl bromide as above, the corresponding di-α-naphthyl-phenyl-bromomethane is obtained in colorless crystals which melt at 125–127° with decomposition, and loss of hydrobromic acid. The bromide, like the chloride, is unstable and becomes colored on standing. It readily forms an additive compound, $C_{27}H_{19}Br.HBr$, when treated in solution with hydrogen bromide.

Analysis. Calc. for $C_{27}H_{19}Br$: Br, 18.88. Found: 18.54.

The chloride and the bromide form additive compounds with mercuric, stannic, ferric, aluminum and zinc chlorides. The additive compounds all have the same deep purple color and all are unstable, decomposing within a short time with the formation of phenyl-di-α-naphthofluorene; consequently, they could not be isolated in pure form.

Phenyl-di-α-naphthofluorene.—Phenyl-di-α-naphthofluorene was prepared by boiling an acetic acid solution of di-α-naphthyl-phenyl carbinol. The solution assumes a purple color which soon disappears, and the reaction is completed within a few minutes. The fluorene crystallizes from the acetic acid in fine, colorless needles, the yield being almost quantitative; m. p. 273°. It is fairly soluble in benzene, slightly soluble in ether, and very slightly soluble in acetic acid, in alcohol, and in petroleum ether.

Since naphthyl groups manifest a greater tendency than phenyl groups for the formation of fluorene linkings, it was considered probable that the compound obtained from di-α-naphthyl-phenyl carbinol was phenyl-di-α-naphthofluorene (I), and not the isomeric α-naphthyl-chrysofluorene (II).

This view was shown to be correct by preparing phenyl-di-α-naphthofluorene from phenyl-di-α-naphthofluorenol as follows.

(I).   (II).   (III).
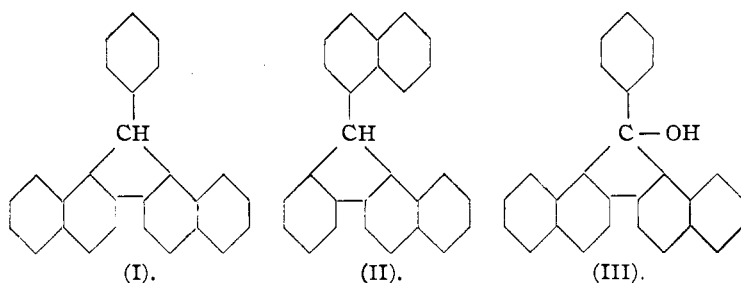
Phenyl-di-α-naphthofluorenol, III.—Di-α-naphthofluorene,[5] prepared from di-α-naphthyl carbinol, was oxidized to di-α-naphthofluorenone,[6] which upon treatment with phenyl-magnesium bromide gave phenyl-di-α-naphthofluorenol in good yield. One g. of magnesium and 5 g. of bromobenzene in ether are allowed to react and the resulting solution of phenyl-magnesium bromide is added to 2.5 g. of di-α-naphtho-fluorenone suspended in 250 cc. of dry benzene. After heating this mixture on the water-bath for 2 hours, the product is decomposed with water and dilute acid, and the benzene-ether layer is dried and concentrated. The carbinol is obtained in colorless needles, m. p. 286°. Yield, about 2 g. The carbinol is somewhat soluble in ether and benzene, slightly soluble in acetic acid and alcohol, and very slightly soluble in petroleum ether. With conc. sulfuric acid, it gives a bluish-green color.

Analysis. Calc. for $C_{27}H_{18}O$: C, 90.47; H, 5.06. Found: C, 90.10; H, 5.10.

The fluorenol is readily reduced by zinc dust and hydrochloric acid in acetic acid solution. 0.5 g. of the fluorenol is dissolved in 100 cc. of acetic acid, 1 g. of zinc dust added, and conc. hydrochloric acid slowly dropped into the boiling solution until a test portion no longer shows a bluish-green coloration with conc. sulfuric acid. A half hour's heating is usually sufficient. The solution is then filtered hot from the excess zinc dust and, as it cools, the phenyl-di-α-naphthofluorene crystallizes in colorless needles. An additional small amount may be obtained by diluting the mother liquid with water and extracting it with benzene. The yield is almost quantitative. The compound is identical with that obtained from di-α-naphthyl-phenyl carbinol and has the same melting point, 273°. Moreover, an intimate mixture of the two compounds showed no change in melting point.

Analyses. Calc. for $C_{27}H_{18}$: C, 94.70; H, 5.30. Found: C, 94.50, 94.33; H, 5.23, 5.22.

Di-α-naphthyl-phenyl-methane.—Elbs[4] obtained di-α-naphthyl-phenyl-methane by distilling either di-α-naphthyl-phenyl carbinol or α-naphthyl-phenyl-β-pinacoline with zinc dust, and describes it as a grayish-yellow powder when crystallized from ether-alcohol, with an indefinite melting point, about 180°. We prepared this hydrocarbon by reducing the carbinol with zinc dust and acetic acid at a temperature of 75–80°. Two and a half g. of the carbinol is dissolved in 100 cc. of acetic acid and 10 g. of zinc dust is added. The mixture is stirred vigorously and heated at 75° until a test portion is no longer colored by conc. sulfuric acid. From 1 to 2 hours' heating is required. (If during the reduction the temperature rises much above 75°, phenyl-di-α-naphtho-fluorene is formed.) The solution is then heated to boiling, filtered, and the residue washed with hot acetic acid. The hydrocarbon is precipitated with water, filtered,

[5] Schmidlin and Massini, *Ber.*, **42**, 2387 (1909); also Chichibabin and Magidson, *J. prakt. Chem.*, **90**, 168 (1914).

[6] Schmidlin and Huber, *Ber.*, **43**, 2833 (1910).

dried, and recrystallized from acetic acid or ether. Very fine, colorless needles are obtained. Yield, about 90%; m. p. 204°. It is soluble in benzene, fairly soluble in ether, and very slightly soluble in acetic acid, in alcohol, and in petroleum ether.

Analyses. Calc. for $C_{27}H_{20}$: C, 94.14; H, 5.86. Found: C, 93.80, 93.66; H., 5.83, 5.86.

Di-α-naphthyl-phenyl-aminomethane.—Di-α-naphthyl-phenyl-aminomethane was prepared by passing dry ammonia into a solution of di-α-naphthyl-phenyl-chloromethane or -bromomethane, the latter reacting more readily. Five g. of di-α-naphthyl-phenyl carbinol, dissolved in benzene, is treated with 5 g. of acetyl bromide, and, after standing for 10 to 15 minutes, the solution is thoroughly saturated with dry ammonia. The precipitated ammonium salts are filtered off and the solution is evaporated. Upon addition of ether, the amine is obtained in very fine, colorless crystals. Yield, about 80%. It is soluble in benzene and in chloroform, and but very slightly soluble in ether, in alcohol, and in petroleum ether. The crystals turn brown at about 200° and melt with decomposition at 205–210°, depending on the rate of heating. Upon treatment of the amine with nitrous acid, the carbinol is obtained.
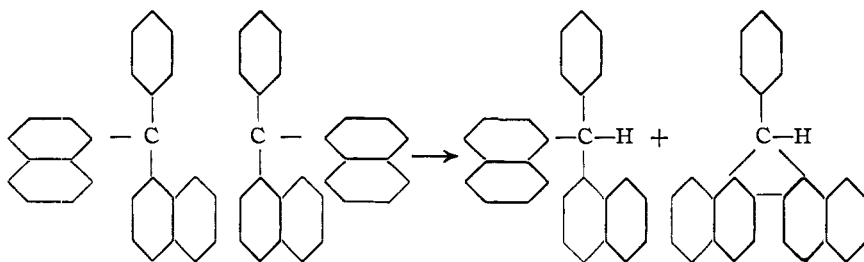
Di-α-naphthyl-phenyl-methyl.

Preparation.—Di-α-naphthyl-phenyl-methyl was prepared by shaking a solution of di-α-naphthyl-phenyl-chloromethane with molecular silver in the absence of air. The solution of the free radical has a deep reddish-brown color similar to that of α-naphthyl-diphenyl-methyl solutions, but more intense. However, the di-α-naphthyl-phenyl-methyl in solution is unstable and the color gradually fades, even when carefully protected from light, until, after a few weeks, it has practically disappeared, although the solution never becomes entirely colorless. All attempts to isolate the free radical in pure form were unsuccessful, although a number of solvents were tried, *e. g.*, benzene, ether, carbon disulfide, and acetone.

Auto-reduction of the Free Radical.—Solutions of the free radical which were allowed to stand until decolorized were always found to contain considerable amounts of di-α-naphthyl-phenyl-methane, which would suggest a reaction similar to the auto-reduction of triphenyl-methyl under the influence of light to give triphenyl-methane and di-biphenylene-diphenylethane.[7] Three g. of di-α-naphthyl-phenyl-chloromethane and 3 g. of molecular silver were placed in a 100cc. bottle and enough dry benzene was added almost to fill the bottle, which was then tightly corked. After shaking this mixture for 12 hours, the bottle was allowed to stand for one month protected from the light, by which time almost all of the color of the free radical had disappeared. The silver chloride and excess silver were then filtered off, the benzene evaporated and the residue taken up in ether. Concentration of this solution gave 1.2 g. of di-α-naphthyl-phenyl-methane, and a dark red oil which could not be crystallized.

The same experiment was carried out with ether as the solvent in place of benzene. In this case, phenyl-di-α-naphthofluorene was isolated

[7] Schmidlin and Garcia-Banus, *Ber.*, **45**, 1344 (1912).

from the solution, in addition to di-α-naphthyl-phenyl-methane, and the same oily residue was obtained. (The fluorene is less soluble in ether than di-α-naphthyl-phenyl-methane and is the first to crystallize.) This would seem to indicate that part of the free radical in solution reacts as follows.


Action of Oxygen.—Although a solution of di-α-naphthyl-phenyl-methyl absorbs oxygen and is decolorized, attempts to isolate the corresponding peroxide were unsuccessful. The absorption is rapid at first and the solution becomes practically colorless; then a further gradual absorption takes place for several hours and the solution assumes a dark reddish color. The amount of oxygen absorbed is approximately 150% of that required for the formation of the peroxide, indicating more or less complex decomposition.

One g. of di-α-naphthyl-phenyl-chloromethane in bromobenzene, and 2 g. of molecular silver were sealed in a test-tube and shaken for 12 hours. Upon breaking the tube and exposing to air in the absorption apparatus, which has been described in a previous paper,[8] 47 cc. of oxygen (corrected to standard conditions) was absorbed in the course of 3 hours. The amount required theoretically for the formation of the peroxide is 32.8 cc. When the sample is allowed to stand for any considerable length of time after its preparation, the absorption decreases in proportion to the time which has elapsed but never becomes zero. A sample of the free radical in benzene, prepared by shaking 1.00 g. of the chloride with 2 g. of molecular silver in a sealed tube, was allowed to stand for a month protected from light, by which time the color of the free radical had practically disappeared. Nevertheless, it still absorbed 15 cc. of oxygen in the course of 3 hours. It appears, therefore, that the peroxide and one or more products obtained from the auto-reduction of the free radical are unstable and decompose on exposure to air with the absorption of oxygen.

Action of Hydrochloric Acid.—When a solution of di-α-naphthyl-phenyl-methyl is treated with hydrochloric acid in the absence of air, decolorization takes place within a few hours and the resultant colorless

[8] Ref. 2, p. 1661.

solution contains di-α-naphthyl-phenyl-methane and **di-α-napthyl-phenyl-chloromethane.**
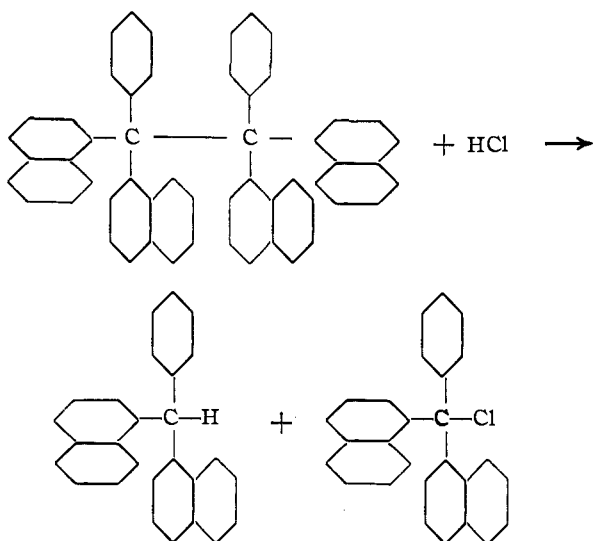
Consequently, when di-α-naphthyl-phenyl-chloromethane is shaken with excess of molecular silver in benzene which is saturated with gaseous hydrochloric acid, the di-α-naphthyl-phenyl-methyl which is formed immediately reacts with the hydrochloric acid to give the methane and the chloride as above; the latter then reacts with the excess of molecular silver to form more of the free radical and so on to completion. Two and a half g. of chloride and 5 g. of molecular silver were shaken in benzene saturated with hydrochloric acid. About 10–12 hours was required for the complete disappearance of the color of the free radical. Two and a tenth g. of di-α-naphthyl-phenyl-methane (92.5% yield) was obtained upon concentrating the benzene solution and adding petroleum ether. No other compounds could be isolated from the solution.

Summary.

1. Di-α-naphthyl-phenyl carbinol and the corresponding chloride, bromide, amine, methane, fluorene, and fluorenol have been synthesized and described.

2. Di-α-naphthyl-phenyl-methyl has been prepared in solution and found to be unstable. The auto-reduction, and the action of oxygen and of hydrochloric acid upon the free radical are discussed.

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