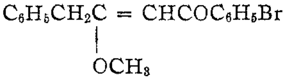
The oil was distilled with steam and hydrolyzed with potassium hydroxide. It gave a solid acid which melted at 76°. A mixture of the substance and phenyl acetic acid likewise melted at this temperature. The oily oxidation product was, therefore, methyl phenylacetate.

The solid left behind after removing the ester by steam distillation proved to be unchanged substance, and the acid obtained by treating the salts and oxides of manganese with sodium hydrogen sulfite and dilute acid was identified as bromo-benzoic acid. These oxidation products —methyl phenylacetate and *p*-bromo-benzoic acid—show that the formula of the methoxy compound must be



$$\underset{\displaystyle OCH_3}{C_6H_5CH_2\overset{}{C}} = CHCOC_6H_5Br$$

**Phenacetyl-(4-bromobenzyl) Methane,** $C_6H_5CH_2COCH_2COC_6H_4Br$.—The methoxyl compound is easily hydrolyzed when boiled with a few drops of hydrochloric acid in aqueous alcohol. The product separated, on cooling, in rhombic plates melting at 80–1°.

Calc. for $C_{17}H_{15}O_2Br$: C, 60.5; H, 4.1. Found: C, 60.4; H, 4.3.

The diketone is readily soluble in all common organic solvents except ligroin. When its ethereal solution is shaken with an aqueous solution of copper acetate it forms a pale green copper derivative which is sparingly soluble in ether but dissolves fairly readily in benzene. The diketone can be obtained directly from any of the cyclopropane derivatives by dissolving it with alcoholic sodium hydroxide, acidifying, extracting with ether, and precipitating the diketone as copper derivative.

CAMBRIDGE, MASS.

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

# TRIPHENYLMETHYL. XXIX. A STUDY OF THE PROPERTIES OF DIPHENYL-α-NAPHTHYLMETHYL.

BY M. GOMBERG AND C. S. SCHOEPFLE.[1]

Received July 22, 1919.

## 1. Introduction.

Although the existence of a large number of triarylmethyls has been established, the various investigators in this field have been content to prepare the free radicals in solution only and to show that such solutions on exposure to air give rise to the corresponding peroxides. In a limited number of cases the triarylmethyls were actually isolated and the molecular weight of the free radical determined, and in a few instances absorption spectra have been taken. But in no case except that of triphenylmethyl have the chemical and physical properties of the free

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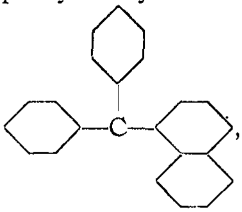
[1] The work described in this article and in the article published in THIS JOURNAL, 39, 1652 (1917), forms part of a thesis presented by C. S. Schoepfle in partial fulfillment of the requirements for the degree of Doctor of Science in the University of Michigan.

radical been thoroughly investigated. The question arises: Are all the peculiar physical and chemical properties of triphenylmethyl characteristic of the triarylmethyls as a class, or do some of them apply only to certain individuals in this class? It therefore seemed desirable to study carefully and fully other members of the triarylmethyls, and thus compare their properties and reactions with those of triphenylmethyl. For this purpose the radical diphenyl-α-naphthylmethyl, , was chosen as it is readily prepared and can be obtained in very pure state. Moreover, it gave promise of most interesting results for it was known, according to preliminary experiments,[1] to exist in solution largely in the mono-molecular phase. Being thus much more highly dissociated, diphenyl-α-naphthylmethyl presumably should show a correspondingly greater degree of unsaturation than triphenylmethyl, and should exhibit a greater reactivity than the latter. In what way would this affect the peroxide factor, and the equilibrium with iodine? And would this free radical give additive compounds more stable than those given by triphenylmethyl? Would it isomerize under the influence of hydrochloric acid similarly to triphenylmethyl?

The exact knowledge of the molecular state of diphenyl-α-naphthylmethyl was considered of utmost importance, since it is the tendency towards dissociation into half-molecules that imparts to the hexa-arylethanes their distinctive reactivity. A comparison of the molecular state of aggregation of diphenyl-α-naphthylmethyl with that of triphenylmethyl should permit one to judge whether the extent of actual dissociation, *i. e.*, the relative amount of free radical actually present, is really the cause for the difference in chemical reactivities of the triarylmethyls among themselves.

The molecular state of these compounds has received more attention than any other single attribute, for the reason that this was supposed to furnish the conclusive answer to the query—can carbon function in the trivalent state? But the number of free radicals, the molecular state of which has been determined with exactness, is after all limited. None the less, it may be considered at the present time as fairly well established that the molecular state of triarylmethyls is best represented by the general expression which covers both the tautomerization phenomenon and the dissociation phenomenon:[2]

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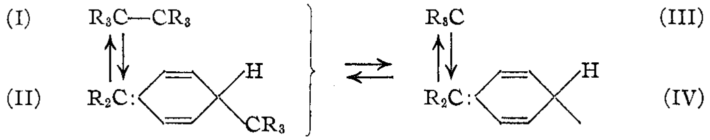
[1] THIS JOURNAL, 39, 1668 (1917).

[2] *Ber.*, 46, 228 (1913).



In other words, there is a tautomeric equilibrium between two dimolecular modifications, the benzenoid hexa-aryl ethane (I) and its quinonoid modification (II); also between two monomolecular modifications, the benzenoid triarylmethyl (III), wherein the central carbon atom is trivalent, and the quinonoid modification (IV), in which the *para*-carbon atom assumes the trivalent state. The experimental evidence upon which is based the assumption of the existence of a tautomeric pair in the dimolecular and in the monomolecular phases of the triarylmethyls has been dealt with in previous papers. The validity of that evidence has not been impaired, in our opinion, by any subsequent results. The new experimental evidence contributed in this paper deals with the dissociation phenomenon only and has no direct bearing on the tautomerism phenomenon. For this reason, the tautomerism question will be left out of consideration for the sake of simplicity in the following discussion; the dissociation phenomenon alone will be considered, and as if occurring only in the following sense:

$$R_3C — CR_3 \rightleftarrows 2R_3C.$$

**Factors Influencing Degree of Dissociation.**—It is evident that the extent of the dissociation must differ, primarily, with the nature of the free radical. Triphenylmethyl exists largely in the dimolecular state, but triarylmethyls containing biphenyl groups are monomolecular to the extent of 15%, 80%, and 100%, respectively, according to the number of biphenyl groups in the molecule.[1] The hypothesis, however, that the dissociation of the hexa-aryl ethanes is proportional to the complexity of the aryl groups has been shown to be untenable. From the study of the molecular weights of a selected group of triarylmethyls it was found impossible to formulate the relation between the complexity of the aryl groups on the one hand and the tendency of these ethanes towards dissociation into free radicals on the other.[2]

Other factors which may influence the equilibrium between the monomolecular and the dimolecular modifications in solution, are the nature of the solvent, the concentration of the solute, and the temperature of the solution. The question as to whether the nature of the solvent exerts an influence on the extent of dissociation could only be finally settled by a set of molecular weight determinations on a given triarylmethyl in

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[1] Schlenk, Weickel and Herzenstein, *Ann.*, 394, 186 (1912); *Ber.*, 43, 1756 (1910); *Ann.*, 372, 4 (1909); Schmidlin and Garcia-Banus, *Ber.*, 45, 3176 (1912).

[2] THIS JOURNAL, 39, 1672 (1917).

various solvents which freeze approximately at the same temperature. But it is doubtful whether this factor is of appreciable influence, barring of course such instances where chemical combination between solute and solvent occur. We have assumed that this influence is practically negligible, and the results herein described support this assumption.

Piccard,[1] Schmidlin,[2] and others have studied by different methods the effect of the concentration upon the degree of dissociation of the hexa-arylethane in solution. The writers[3] have determined with painstaking accuracy the molecular weight of 7 different triarylmethyls in naphthalene as a solvent, with concentrations ranging from 1 to 6%. The results obtained show unmistakably that, in every case, the dissociation of the hexa-aryl ethanes into free radicals increases with dilution of the solute, and in some cases reaches 100%. It remained to study the third factor which must influence the equilibrium between the monomolecular and the dimolecular phase of the free radical, namely the effect of temperature. Some work in this respect has been done in the past, but mostly of qualitative nature.[4] We have now, with this end in view, determined very carefully the molecular weight of diphenyl-$\alpha$-naphthylmethyl in a number of different solvents whose freezing points cover a wide range of temperature, 5° to 80°. The results, it is believed, settle the mooted question as regards the decided increase of dissociation with increase of temperature, at least in the instance of this particular free radical.

The object, then, of this investigation has been: (1) having selected a compound possessing a considerably greater degree of dissociation than triphenylmethyl, to determine whether this attribute would be accompanied by an enhancement of the various chemical characteristics typical to triphenylmethyl; (2) to determine with a high degree of accuracy the molecular weight of this free radical in various solvents covering a wide range of temperature, in order to ascertain the influence of temperature on the molecular state of the free radical.

## 2. Chemical Reactions of Diphenyl-$\alpha$-naphthylmethyl.

**Preparation of Diphenyl-$\alpha$-naphthylmethyl Chloride.**—Attempts were made to prepare the required diphenylnaphthylmethyl chloride by the Friedel and Crafts' reaction, condensing benzophenone chloride with naphthalene. The diphenylnaphthylmethyl chloride thus obtained is almost colorless, and upon one recrystallization melts sharply at 169°. The yield, however, is never more than 20%. The use of ferric chloride in place of aluminium chloride gave no better results.

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[1] *Ann.*, **381**, 347 (1911).

[2] "Das Triphenylmethyl," Ferdinand Enke, 1914, p. 67.

[3] This Journal, **39**, 1664 (1917).

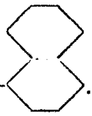
[4] Schlenk and Mair, *Ann.*, **394**, 179 (1912); Schmidlin, *Ber.*, **45**, 3180 (1912).

An attempt was next made to apply a modified Grignard reaction, namely to combine benzophenone chloride with α-naphthyl magnesium bromide. But this gave an impure product which could not be crystallized either as the carbinol or the chloride even after purification by boiling with charcoal. Consequently it was decided to revert to the regular Grignard reaction, employing benzophenone and α-naphthyl magnesium bromide. This gives about an 80% yield of diphenylnaphthyl carbinol. To obtain the corresponding chloride, the carbinol is dissolved in benzene and the amount of acetyl chloride required to replace the hydroxy group by chlorine is added. Upon concentrating the solution, the diphenylnaphthylmethyl chloride is obtained in large, colorless crystals which melt at 170–171°. The product was always recrystallized from benzene to remove any traces of acid.

If the solution of diphenyl-α-naphthyl carbinol is treated with acetyl bromide in place of acetyl chloride, the corresponding bromide is formed. The crystals are colorless and melt at 165–166°, with slight decomposition. The bromide is quite stable and agrees with the chloride in all its properties.

Calc. for $C_{23}H_{17}Br$: Br, 21.4. Found: 21.6.

By treating a solution of diphenyl-α-naphthylmethyl chloride in absolute alcohol with sodium ethoxide, or by passing hydrogen chloride into an alcoholic solution of either the carbinol or the chloride, diphenylnaphthyl ethyl ether is obtained in well-defined, colorless crystals which melt at 132°.

**The Free Radical,** $(C_6H_5)_2C$—  .—To prepare the free radical, 4 g. of diphenyl-α-naphthylmethyl chloride and 4 g. of molecular silver are placed in a 100 cc. bottle, and enough dry benzene added to almost fill the bottle which is then tightly corked. After several hours' shaking, the reaction is complete. The cork is now removed, and there is quickly inserted the glass connection which permits the siphoning off of the clear liquid into the standard apparatus which has been fully described in previous papers.[1] The benzene is distilled off under reduced pressure and the product recrystallized from hot acetone, air of course being excluded. The solvent is drawn off and the crystalline diphenylnaphthylmethyl is washed several times with acetone, and then dried under reduced pressure in a slow stream of carbon dioxide, the crystals remaining all the while in the same apparatus. As a rule, from 1.5 to 2 g. of the free radical was obtained, the yield being sacrificed to favor a purer product.

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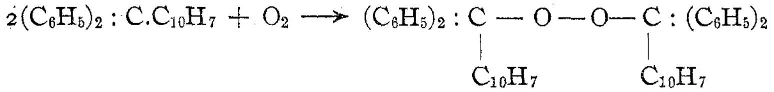
[1] Gomberg and Cone, *Ber.*, **37**, 2033 (1904); Gomberg and Schoepfle, THIS JOURNAL, **39**, 1659 (1917).

The solution of diphenylnaphthylmethyl has a deep reddish brown color, but the crystals obtained are practically colorless, becoming light yellow upon standing. When heated in an atmosphere of carbon dioxide, they turn brown at about 130° and melt at 135–137°, although the melting point is not sharp.

**Action of Oxygen.**—When the deeply colored solution of diphenylnaphthylmethyl is exposed to oxygen or air it is rapidly decolorized and a crystalline peroxide is formed. Diphenylnaphthylmethyl peroxide is practically insoluble in ether, petroleum ether or benzene, but is slightly soluble in hot carbon disulfide from which it crystallizes in very fine, colorless crystals, melting at 172–173° with decomposition.

In the formation of the peroxide, the theoretical amount of oxygen is absorbed in accordance with the equation:



$$2(C_6H_5)_2:C.C_{10}H_7 + O_2 \longrightarrow (C_6H_5)_2:\underset{\displaystyle C_{10}H_7}{\underset{|}{C}}-O-O-\underset{\displaystyle C_{10}H_7}{\underset{|}{C}}:(C_6H_5)_2$$

The apparatus used in measuring the absorption of oxygen by triarylmethyls has been described in detail in a previous paper.[1] It consists of a 175 cc. absorption bottle which is connected with a water-jacketed gas buret provided with a leveling tube containing bromobenzene. A weighed sample of diphenylnaphthylmethyl chloride and an equal amount of molecular silver are put in a small test tube which is then filled with bromobenzene and quickly sealed. After several hours' shaking, the tube is placed in the absorption bottle, covered with about 25 cc. of bromobenzene, and the bottle sealed with paraffin and submerged in a large pail of water which is kept at the desired temperature. The apparatus is now filled with dry oxygen, and after the temperature has become constant, the bottle is shaken to break the tube. The absorption is measured by means of the buret, and calculated on the basis that the diphenylnaphthylmethyl chloride taken had given the theoretical amount of free radical. During the course of the experiment, the temperature of the bottle and the buret was kept constant while corrections were applied to allow for changes in barometric pressure.

As in the case of triphenylmethyl, the absorption proceeds at a very rapid rate, being complete within a few minutes if sufficient bromobenzene is used to keep all of the free radical in solution (Expts. 1–3).

We have also determined the amount of oxygen absorbed when the crystalline free radical is similarly treated. The sample in the form of pellets was put in a small test tube which was then filled with bromobenzene and quickly sealed. The amount of absorption was somewhat smaller in this case than in the preceding experiments, doubtless due to a

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[1] This Journal, 39, 1661 (1917).

slight oxidation which took place during the time required for sealing the tube (Expts. 4 and 5).

| | | Wt. of sample. | | Oxygen absorbed.[1] | |
|---|---|---|---|---|---|
| | | Diphenyl-napthylmethyl chloride. G. | Diphenyl-naphthyl-methyl. G. | Cc. | % of calculated. |
| 1 | With oxygen | 1.000 | ... | 33.0 | 97 |
| 2 | With oxygen | 1.013 | ... | 34.2 | 99 |
| 3 | With air | 1.011 | ... | 32.7 | 95 |
| 4 | With oxygen | ... | 1.029 | 36.2 | 92 |
| 5 | With oxygen | ... | 1.142 | 40.7 | 93 |

In spite of the fact that the theoretical amount of oxygen is absorbed, diphenylnaphthylmethyl, like triphenylmethyl, does not give the theoretical amount of peroxide. To determine the amount of peroxide formed, the sample of the free radical was dissolved in ether and oxidized by passing air through the solution. The precipitated peroxide was transferred to a modified Gooch crucible, washed with ether, then dried and weighed.

| | Wt. of diphenyl-naphthylmethyl. G. | Wt. of per-oxide. G. | % of theo-retical amount. |
|---|---|---|---|
| 1 | 1.280 | 1.160 | 86 |
| 2 | 1.251 | 1.133 | 86 |
| 3 | 1.595 | 1.446 | 86 |

Therefore, for diphenylnaphthylmethyl we have a remarkably constant peroxide factor of 86%. If benzene is used as the solvent in place of ether, the factor is somewhat lower varying from 80% to 82%.

**Absorption of Iodine.**—If a solution of iodine in benzene or carbon disulfide is added to a solution of diphenylnaphthylmethyl, the dark color of iodine instantly disappears, and the absorption of iodine continues until approximately 60% of the free radical has been titrated. A weighed sample of diphenylnaphthylmethyl is placed in a bottle from which the air is completely removed by successively exhausting and filling with carbon dioxide. Enough bromobenzene is added to dissolve the free radical (the free radical is more soluble in bromobenzene than in benzene) and then a standard solution of iodine in benzene is slowly added. The deep reddish brown color of the solution gradually becomes lighter and at the equilibrium point, which is fairly distinct, the color changes from the light brown of the free radical to a deep green, the latter color resulting doubtless from the presence of both iodine and the free radical in the solution.

| | Wt. of diphenyl-naphthylmethyl. G. | Cc. of 0.1 $N$ iodine solution absorbed. | % of calculated absorption. |
|---|---|---|---|
| 1 | 2.406 | 50.5 | 61.5 |
| 2 | 2.565 | 49.0 | 56.0 |
| 3 | 2.147 | 46.0 | 63.0 |

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[1] Corrected to standard conditions of temperature and pressure.

Therefore, an equilibrium is established when approximately 60% of the diphenylnaphthylmethyl has been changed to diphenylnaphthylmethyl iodide.

$$(C_6H_5)_2 : C.C_{10}H_7 + I \rightleftarrows (C_6H_5)_2(C_{10}H_7)CI.$$

**Attempts to Isolate the Iodide.**—Attempts were made to isolate the diphenylnaphthylmethyl iodide from the solution obtained by titrating the free radical with a limited amount of iodine as described above, but in no case would the iodide crystallize. Efforts to prepare the iodide by a somewhat different method[1] also proved unsuccessful. 5 g. of diphenylnaphthylmethyl chloride and 2.5 g. of sodium iodide were dissolved separately in acetone, and mixed in an apparatus free from air. The sodium chloride which immediately precipitated out was filtered off and the solution concentrated but the iodide could not be isolated. A considerable amount of diphenylnaphthyl methane was found to be present in the solution, indicating that the free radical, and perhaps the iodide as well, have suffered a change of some sort. The iodide under consideration is therefore even more unstable than triphenylmethyl iodide.

If excess of iodine is added to the solution of the free radical, a dark oil separates out which is undoubtedly a periodide. This periodide could not be crystallized and is apparently unstable, as it is changed into soluble products upon standing for several hours. The resulting solution, as in the above experiments, contains a considerable amount of diphenylnaphthyl methane, and no longer precipitates a peroxide on exposure to air.

That diphenylnaphthylmethyl iodide is actually formed by the action of iodine upon a solution of the free radical, was shown by the preparation of the corresponding anilide. To a solution of 4 g. of diphenylnaphthylmethyl in benzene was added 65 cc. of a 0.1 *N* solution of iodine in benzene, which corresponds to about 50% of the theoretical amount of iodine required to change the free radical into the iodide. 2 g. of aniline was then added, producing an immediate precipitation of aniline hydriodide:

$$(C_6H_5)_2(C_{10}H_7)CI + 2C_6H_5NH_2 \longrightarrow (C_6H_5)_2(C_{10}H_7)C - \underset{H}{N}C_6H_5 + C_6H_5NH_2.HI.$$

After standing for a short time, air was passed through the solution to oxidize the unchanged free radical to the peroxide. The aniline salt and the peroxide were filtered off, the benzene removed under reduced pressure, and the residue taken up in petroleum ether. 2.3 g. of diphenylnaphthylmethyl anilide crystallized, the theoretical yield being 2.5 g. The anilide is obtained in clusters of small, colorless crystals which after several recrystallizations melt at 151°. The compound was found

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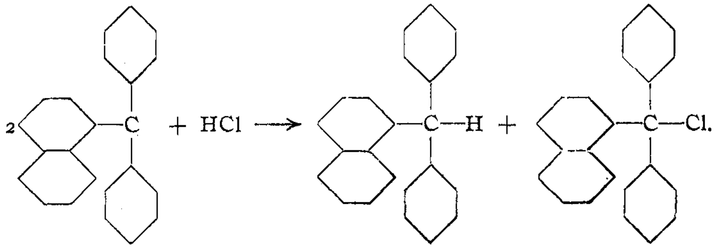
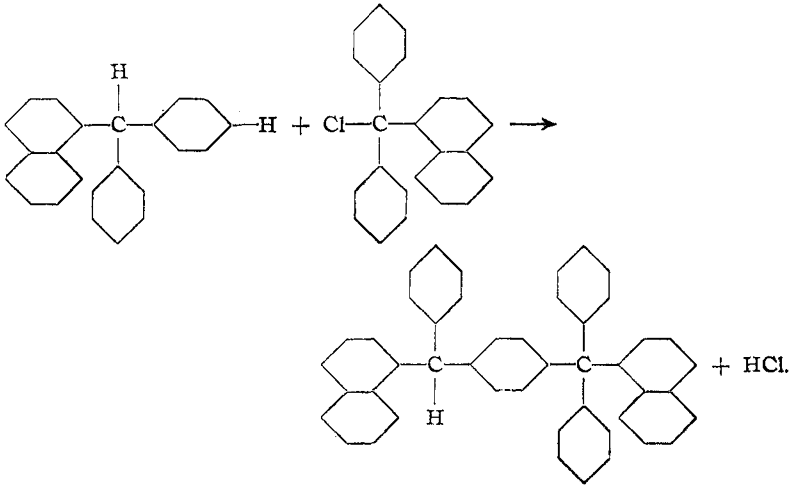
[1] Albrecht, "Das Triphenylmethyl," Schmidlin, Ferdinand Enke, 1914, p. 87.

to be identical with the anilide prepared similarly from diphenylnaphthylmethyl chloride. The anilide is readily decomposed into aniline and diphenylnaphthylmethyl chloride when a benzene solution of it is treated with hydrogen chloride.

**Action of Hydrochloric Acid.**—When a solution of diphenylnaphthylmethyl is treated in the cold with hydrochloric acid, it is decolorized, becoming absolutely colorless in the course of several hours. The resulting solution contains diphenylnaphthyl methane and diphenylnaphthylmethyl chloride, along with a smaller amount of the "polymer" of the free radical, indicating that the following two reactions have occurred:



(1)



(2)

The extent to which each reaction takes place was determined by estimating the amount of diphenylnaphthylmethyl chloride which could be obtained from a definite amount of the free radical. The sample of diphenylnaphthylmethyl, 2.4625 g., prepared as usual, was treated in the absence of air with about 150 cc. of benzene saturated with hydrochloric acid. After the free radical was dissolved and the solution had become colorless, the benzene was removed under reduced pressure; the sample was then redissolved in benzene and again concentrated as far as possible, thus insuring the removal of the excess hydrochloric acid. The chlorine in the residue was estimated in the usual manner. The amount found corresponded to 83% of the amount of diphenylnaphthylmethyl chloride which would have been formed had all the free radical reacted according to Equation 1. Therefore, it may be safely inferred, over 80% of the diphenylnaphthylmethyl reacts to give diphenylnaphthyl methane and diphenylnaphthylmethyl chloride, and the remainder probably reacts according to Equation 2 to form the polymer of diphenylnaphthylmethyl.

To obtain the polymer, 10 g. of diphenylnaphthylmethyl chloride is dissolved in 150 cc. of benzene saturated with hydrochloric acid, and shaken with excess of molecular silver, about 20 g. The solution immediately becomes deeply colored due to the formation of the free radical, and this subsequently reacts with the hydrochloric acid. The diphenylnaphthylmethyl chloride which is formed as one of the products of the action of the hydrochloric acid upon the free radical, is in turn acted upon by the molecular silver, and so on to completion. The solution becomes colorless after several hours' shaking, and contains then only diphenylnaphthyl methane and the polymer, of which the former is present in much the larger amount. The polymer can be readily separated from the diphenylnaphthyl methane by treating the mixture with boiling alcohol, in which the methane compound is fairly soluble and the polymer practically insoluble. The yield is about 3 g.

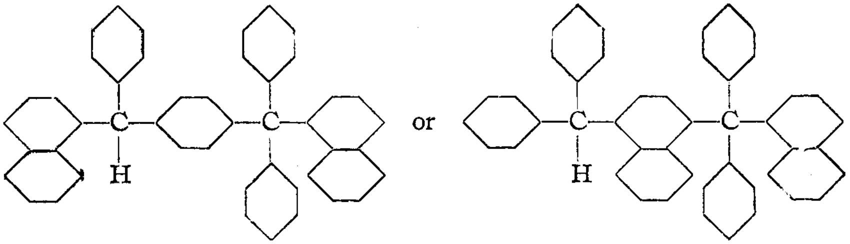
In solubility the polymer is very similar to *p*-benzohydryltetraphenyl methane, which is the principal product when triphenylmethyl is treated with hydrochloric acid.[1] It is readily soluble in hot benzene, slightly soluble in hot acetic acid, and practically insoluble in alcohol, ether, and petroleum ether. It crystallizes from benzene upon the addition of petroleum ether in very fine, colorless crystals which melt at 234–235°.

Calc. for $C_{46}H_{34}$: C, 94.15; H, 5.85. Found: C, 93.81; H, 5.92.

The molecular weight, determined by the cryoscopic method with naphthalene as the solvent, was found to be abnormal. 0.3615 g. of the polymer in 16.86 g. of naphthalene (K = 70.8), gave a depression of 0.354°.

Calc. for $C_{46}H_{34}$: M, 586. Found: M, 429.

No attempt was made to determine which of the two possible structures



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[1] Gomberg, *Ber.*, 35, 3914 (1902); 36, 376 (1903).

should be assigned to this compound, assuming that the polymerization in this case is identical in character with that of triphenylmethyl under similar circumstances.[1]

**Reduction of the Free Radical.**—Although hydrogen itself has no action upon a solution of diphenylnaphthylmethyl, in the presence of a catalyst, such as platinum black, reduction to diphenylnaphthyl methane takes place quite readily. The platinum black for this purpose was prepared by reducing platinum tetrachloride with formaldehyde in an alkaline solution.

A solution of 5 g. of the free radical in benzene was siphoned into a flask filled with hydrogen and containing 0.5 g. of platinum black. The solution, diluted with ether, was stirred vigorously. It absorbed hydrogen readily, becoming completely decolorized in the course of two hours. The platinum was filtered off, the solution concentrated, and the residue taken up in ether from which practically the theoretical amount of diphenylnaphthyl methane crystallized.

**Attempts to Prepare Additive Compounds of the Free Radical.**—In the experiments to form additive compounds of diphenylnaphthylmethyl the procedure followed was similar to that adopted in the preparation of the additive compounds of triphenylmethyl. After the benzene solution of the free radical had been concentrated as far as possible in the apparatus previously described, about 50 cc. was added of the compound, the additive tendency of which was to be investigated, and the clear solution was allowed to crystallize overnight. The mother liquid was drawn off, and the crystals washed and then dried under reduced pressure in a slow stream of carbon dioxide. A sample of the compound, usually from 1.5–2 g., was weighed out in a porcelain boat, placed into a glass tube about 40 cm. long and heated under reduced pressure in an air bath at 80–100° for one to two hours, a slow stream of carbon dioxide being passed at the same time through the tube. The loss in weight of the sample in the boat should represent in each case the amount of the solvent in combination with the free radical, provided combination between the free radical and the solvent had occurred. That the material suffered no appreciable decomposition as the result of the heating, was shown by the fact that at the end of the experiment it still absorbed 80–85% of the theoretical amount of oxygen.

The action of the following solvents was investigated, at least two experiments, and more often three, being carried out with each solvent.

| | |
|---|---|
| Ethers.............................. | Ethyl ether.<br>Amyl-ethyl ether. |
| Esters.............................. | Amyl formate.<br>Ethyl acetate.<br>Amyl acetate. |

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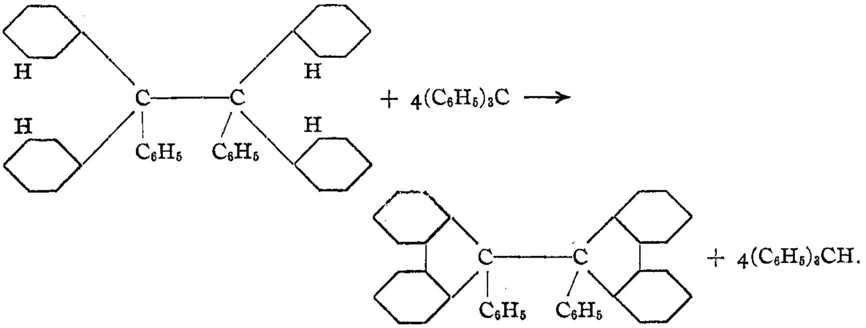
[1] Chichibabin, *Ber.*, 37, 4709 (1904); 41, 2421 (1908).

| | |
|---|---|
| | Ethyl chloroacetate. |
| | Ethyl valerianate. |
| Ketones | Acetone. |
| | Dipropyl ketone. |
| | Methyl-butyl ketone. |
| Nitriles | Acetonitrile. |
| | Propionitrile. |
| Hydrocarbons | Benzene. |
| | Toluene. |
| | Xylene. |
| | Caprylene. |

*No addition of diphenylnaphthylmethyl with any solvent took place. This is in marked contrast to the action of triphenylmethyl.*

**Action of Light.**—A solution of diphenylnaphthylmethyl when exposed to sunlight gradually loses color, the autoöxidation being exceedingly slow. Solutions of the free radical in benzene and bromobenzene which have been exposed to light for 15 months still retain to a slight extent the color of the free radical. This is in contrast to solutions of triphenylmethyl which are quite susceptible to light and become colorless after a few hours' exposure, due to the formation of triphenyl methane and dibiphenylene-diphenyl ethane.[1]



A solution of diphenylnaphthylmethyl which had been exposed to light was found to contain a considerable amount of diphenylnaphthyl methane; it seems probable therefore that the reaction proceeds in a manner similar to that in the case of triphenylmethyl.

## 3. Molecular-Weight Determinations of the Free Radical.

**Apparatus and Manipulation.**—The molecular weight of diphenylnaphthylmethyl was determined by the cryoscopic method using 5 different solvents. The apparatus was of the type devised by Beckmann in which a 2-ring stirrer is used, the upper ring being of wrought iron covered with platinum. This is attracted by an electromagnet attached on the outside of the freezing vessel, and rises and falls due to the alternate

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[1] Gomberg and Cone, *Ber.*, 37, 3546 (1904); Schmidlin and Garcia-Banus, *Ibid.*, 45, 1345 (1912).

making and breaking of the current, effected by a metronome. The apparatus, as adapted by us for the purpose of the molecular-weight determination of triarylmethyls, has been described in detail in a previous paper.[1] The manipulation for the handling and introducing of the free radicals as there described has also been followed in the present case, with hydrogen as the inert gas to guard against oxidation.

**Selection of Solvents.**—Since the primary object of these experiments was to obtain the molecular weight of diphenylnaphthylmethyl at different temperatures, it was attempted to select a series of solvents whose freezing points varied uniformly from 0° to about 90°. The selection of such a series proved extremely difficult, since, in the first place, the free radical is but slightly soluble in many of the solvents ordinarily suitable for cryoscopic determinations, especially those freezing at fairly low temperatures, and secondly, many of the more common solvents do not lend themselves sufficiently to the degree of accuracy required. For example, ethylene dibromide, dimethyl aniline, dimethyl oxalate and benzene can not be used because of the slight solubility of the free radical in these solvents.[2] α-Bromonaphthalene, benzophenone, *m*-bromonitrobenzene, and azobenzene were found to be unsuited for accurate determinations, due partly to the readiness with which they supercool, and partly to the fact that from 5 to 8 minutes are required after the solution has started to freeze for the temperature to reach the highest point. Still another difficulty was encountered in the case of *p*-dibromobenzene. Although this proved to be an excellent solvent and in general well suited for accurate determinations, it was found that the freezing point of the solution of the free radical did not remain constant but rose steadily with successive determinations showing that some manner of decomposition was taking place, due probably to the relatively high temperature of its freezing point, 87°. Therefore, experiments with this solvent were necessarily abandoned.

After considerable preliminary investigation, the following series of solvents were selected:

| | F. P. |
|---|---|
| Nitrobenzene | 6° |
| *p*-Bromotoluene | 27° |
| *p*-Dichlorobenzene | 53° |
| *p*-Chlorobromobenzene | 65° |
| Naphthalene | 80° |

All these solvents were very carefully distilled, and in addition the *p*-

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[1] This Journal, 39, 1662 (1917).

[2] Schlenk and Renning (*Ann.*, 394, 194 (1912)), have determined the molecular weight of diphenyl-α-naphthylmethyl in benzene by the cryoscopic method, obtaining values of 363 and 372 with concentrations of 2.4% and 2.8%, respectively. But we were unable to obtain even a 2% concentration of the free radical in benzene at the temperature of its freezing point, 6°.

dichlorobenzene and *p*-chlorobromobenzene were crystallized from alcohol.

The molecular depression constant of each solvent was determined for this particular apparatus and under exactly the same conditions that were to prevail in the experiments to follow, using as the solute triphenyl methane which had been painstakingly purified by repeated crystallization from alcohol and benzene. No correction was applied to the weight of the solvent to account for the amount which solidifies due to the supercooling and thereby decreases the actual quantity of material functioning as a solvent. For the supercooling was fairly uniform as a rule, and consequently this error is automatically taken care of to a large extent by the molecular depression constant of the solvent which was determined with approximately the same degree of supercooling.

The samples used for molecular-weight determinations were dried carefully in the manner previously described, and in addition, were heated under reduced pressure in a slow stream of carbon dioxide for one hour at a temperature of 50 to 60°, to insure the removal of all traces of solvent. As a rule, 3 additions were made which provided concentrations ranging from 1% to 3–4%.

Determination of the Molecular Depression Constants with $(C_6H_5)_3CH$ (244.1).

| Solvent. | Solvent. G. | Triphenyl-methane. G. | Concentration. %. | Depression of freezing point. | Constant. |
|---|---|---|---|---|---|
| 1 Nitrobenzene | 23.39 | 0.2175 | 0.93 | 0.273 | 71.7 |
| | ... | 0.4262 | 1.82 | 0.530 | 71.0 |
| | ... | 0.6349 | 2.71 | 0.782 | 70.3 |
| | | | | Av., | 71.0 |
| 2 *p*-Bromotoluene | 26.54 | 0.2817 | 1.06 | 0.366 | 84.2 |
| | ... | 0.5238 | 1.97 | 0.680 | 84.1 |
| | ... | 0.7826 | 2.95 | 1.013 | 83.9 |
| | | | | Av., | 84.1 |
| 3 *p*-Dichlorobenzene | 19.86 | 0.2308 | 1.16 | 0.372 | 78.1 |
| | ... | 0.4721 | 2.38 | 0.741 | 76.1 |
| | ... | 0.7151 | 3.60 | 1.106 | 75.0 |
| | | | | Av., | 76.4 |
| 4 *p*-Chlorobromobenzene | 24.60 | 0.2889 | 1.17 | 0.486 | 101.0 |
| | ... | 0.6033 | 2.45 | 1.003 | 99.8 |
| | ... | 0.9213 | 3.75 | 1.519 | 99.0 |
| | | | | Av., | 99.9 |
| 5 Naphthalene | 17.66 | 0.2706 | 1.53 | 0.446 | 71.1 |
| | ... | 0.5408 | 3.06 | 0.889 | 70.9 |
| | ... | 0.8077 | 4.57 | 1.320 | 70.5 |
| | | | | Av., | 70.8 |

DETERMINATION OF THE MOLECULAR WEIGHT OF DIPHENYL-α-NAPHTHYLMETHYL.

| Solvent. | F. p. | Solvent. G. | Diphenyl-naphthyl-methyl. G. | Concentration. %. | Depression of freezing point. | Molecular weight. |
|---|---|---|---|---|---|---|
| 1 Nitrobenzene | 6° | 23.23 | 0.2136 | 0.92 | 0.195 | 334.8 |
| | ... | ... | 0.4136 | 1.78 | 0.369 | 342.6 |
| | ... | ... | 0.6298 | 2.71 | 0.552 | 348.7 |
| | ... | 24.00 | 0.2150 | 0.90 | 0.194 | 327.9 |
| | ... | ... | 0.4229 | 1.76 | 0.368 | 340.0 |
| | ... | ... | 0.6424 | 2.68 | 0.542 | 350.6 |
| | ... | 23.41 | 0.2179 | 0.93 | 0.201 | 328.8 |
| | ... | ... | 0.4247 | 1.81 | 0.373 | 345.3 |
| | ... | ... | 0.6297 | 2.69 | 0.540 | 353.7 |
| 2 *p*-Bromotoluene | 27° | 26.56 | 0.2367 | 0.89 | 0.245 | 305.9 |
| | ... | ... | 0.5084 | 1.91 | 0.487 | 330.6 |
| | ... | ... | 0.7869 | 2.96 | 0.736 | 338.5 |
| | ... | 26.48 | 0.2485 | 0.94 | 0.257 | 307.1 |
| | ... | ... | 0.4992 | 1.89 | 0.483 | 328.2 |
| | ... | ... | 0.7327 | 2.77 | 0.692 | 336.3 |
| | ... | 26.71 | 0.2645 | 0.99 | 0.264 | 315.5 |
| | ... | ... | 0.5075 | 1.90 | 0.482 | 331.5 |
| | ... | ... | 0.7400 | 2.77 | 0.686 | 339.7 |
| 3 *p*-Dichlorobenzene | 53° | 20.01 | 0.2209 | 1.10 | 0.292 | 288.8 |
| | ... | ... | 0.4672 | 2.33 | 0.582 | 306.5 |
| | ... | ... | 0.7217 | 3.61 | 0.862 | 319.7 |
| | ... | 19.90 | 0.2326 | 1.17 | 0.308 | 289.9 |
| | ... | ... | 0.4876 | 2.45 | 0.603 | 310.4 |
| | ... | ... | 0.7423 | 3.73 | 0.878 | 324.6 |
| | ... | 19.89 | 0.2313 | 1.16 | 0.313 | 283.9 |
| | ... | ... | 0.4623 | 2.32 | 0.578 | 307.2 |
| | ... | ... | 0.7198 | 3.62 | 0.854 | 323.7 |
| 4 *p*-Chlorobromobenzene | 65° | 24.51 | 0.2748 | 1.12 | 0.410 | 273.2 |
| | ... | ... | 0.6025 | 2.46 | 0.827 | 296.9 |
| | ... | ... | 0.9520 | 3.88 | 1.257 | 308.7 |
| | ... | 24.72 | 0.2665 | 1.08 | 0.397 | 271.3 |
| | ... | ... | 0.6116 | 2.47 | 0.839 | 294.6 |
| | ... | ... | 0.9626 | 3.89 | 1.263 | 308.0 |
| | ... | 24.66 | 0.2915 | 1.18 | 0.423 | 279.2 |
| | ... | ... | 0.6178 | 2.51 | 0.836 | 299.4 |
| | ... | ... | 0.9577 | 3.88 | 1.241 | 312.6 |
| 5 Naphthalene[1] | 80° | 17.88 | 0.2175 | 1.22 | 0.336 | 256.3 |
| | ... | ... | 0.4445 | 2.49 | 0.667 | 263.9 |
| | ... | ... | 0.7125 | 3.98 | 1.035 | 272.6 |
| | ... | 18.06 | 0.2136 | 1.18 | 0.329 | 254.5 |
| | ... | ... | 0.4402 | 2.44 | 0.649 | 265.9 |
| | ... | ... | 0.7073 | 3.92 | 1.016 | 272.9 |
| | ... | 17.96 | 0.1976 | 1.10 | 0.304 | 256.2 |
| | ... | ... | 0.4387 | 2.44 | 0.655 | 264.0 |
| | ... | ... | 0.6982 | 3.89 | 1.011 | 272.2 |

[1] THIS JOURNAL, 39, 1670 (1917).

Successive determinations showed that the freezing point of the solution of any definite concentration remained perfectly constant. This shows that no decomposition was taking place, and together with the fact that no hydrogen was being absorbed, is sufficient proof that no reduction of the free radical to diphenylnaphthyl methane was occurring in virtue of the possible catalytic effect of the platinum stirrer. As a further check, at the end of the experiment ether was added to the solution and air passed through it. From 80–82% of the peroxide was obtained instead of the usual 86%, offering in this way conclusive evidence that the free radical undergoes no change during the molecular-weight determination. In the following table, each experiment represents an individual preparation, and thus in no case were two determinations of the molecular weight made upon the same sample. Also, the sample was never more than one day old, the free radical being prepared in the afternoon, allowed to crystallize overnight, isolated the following morning and the molecular weight taken the same afternoon.

In the following diagram the results of the molecular-weight determinations are plotted in the form of curves, using the concentrations as abscissas and the values of the molecular weight as ordinates. (The molecular weight calculated for $(C_6H_5)_2(C_{10}H_7)C$ is 293.)

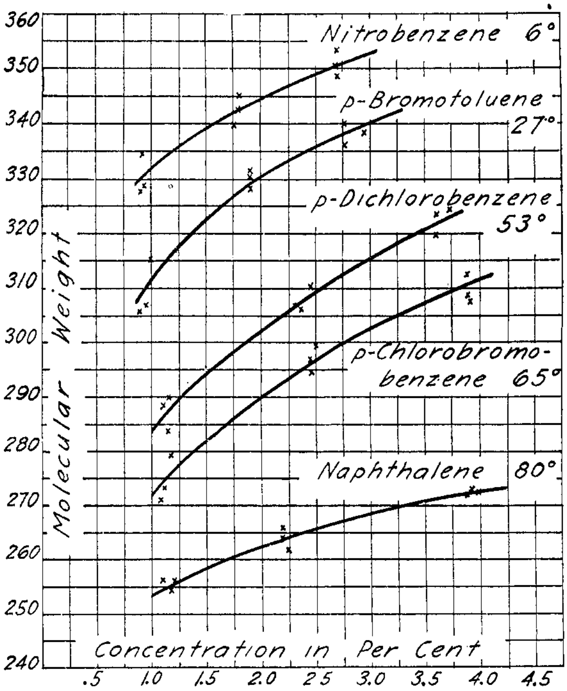


Fig. 1.

## 4. Discussion of Results.

Solutions of diphenyl-α-naphthylmethyl possess intense color, much more so than those of triphenylmethyl, but in the solid state both free radicals are almost wholly devoid of color. Attention has been called in a previous paper, and it is emphasized again, that in the opinion of the writers, "Not dissociation alone into triarylmethyl, but, in addition, the consequent tautomerization of this into its quinonoid modification constitute a satisfactory explanation of the color phenomena."

The oxidation of diphenylnaphthylmethyl is similar in every respect to the oxidation of triphenylmethyl. In both instances there is equally rapid absorption and the theoretical amount of oxygen required to form the peroxide is absorbed, and in each case, approximately the same empirical peroxide factor of 86% is obtained.

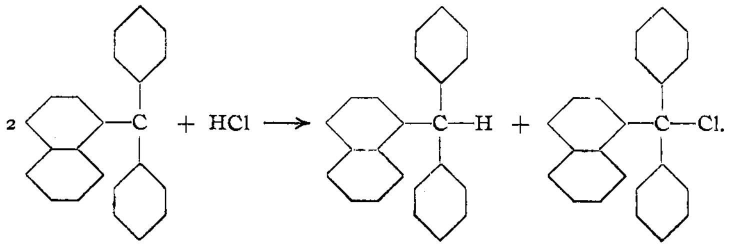
With iodine, diphenylnaphthylmethyl, like triphenylmethyl, reacts to form the corresponding iodide. But if the absorption of iodine is a measure of the degree of unsaturation, *i. e.*, the degree of dissociation into the monomolecular state, then the titration of the free radical to the iodide should proceed more nearly to completion with diphenylnaphthylmethyl than with triphenylmethyl. In reality, however, an equilibrium is reached when only 60% of the diphenylnaphthylmethyl has been transformed into the iodide, while the equilibrium with triphenylmethyl is not reached until 80% of the free radical has been titrated. It is evident that although the absorption of iodine shows the presence of a free radical, it does not serve as an indication of the extent to which the free radical exists in the monomolecular state. The reaction is more complex than one of simple addition between the free radical and iodine, as it involves a mobile equilibrium between the dimolecular and the monomolecular phases of the free radical as well as a mobile equilibrium between the monomolecular free radical and the resulting iodide, the limiting values of the latter equilibrium depending primarily upon the stability of the iodide and its tendency to dissociate.

$$R_3C - CR_3 \rightleftarrows 2R_3C.$$

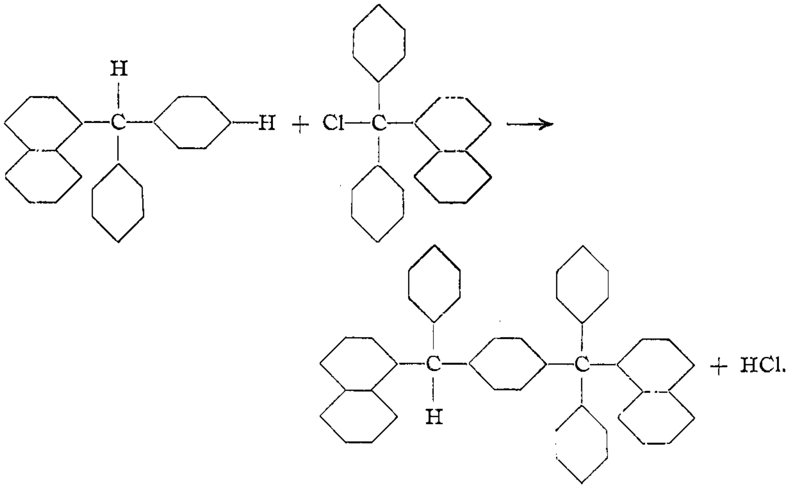
$$R_3C + I \rightleftarrows R_3CI.$$

The action of hydrochloric acid upon a solution of diphenylnaphthylmethyl confirms in a measure the explanation advanced by Chichibabin to account for the production of *p*-benzohydryltetraphenyl methane by the action of hydrochloric acid upon triphenylmethyl. Two reactions take place simultaneously.

Triphenylmethyl reacts largely to form the polymer, *p*-benzohydryltetraphenyl methane, but 6% of triphenyl methane and triphenylmethyl chloride being formed; with diphenylnaphthylmethyl, however, the opposite is true, for in this case over 80% of the free radical goes to form diphenylnaphthyl methane and diphenylnaphthylmethyl chloride, the

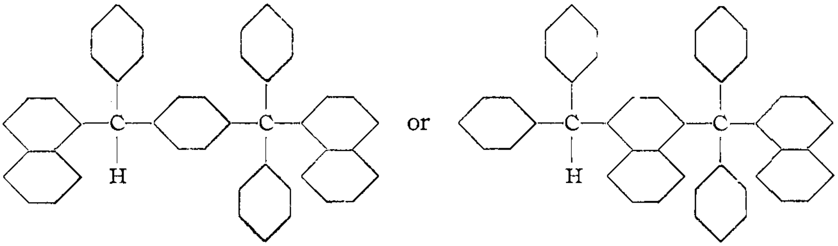


(1)



(2)

remainder condensing to give the polymer. This polymer, which is perfectly stable and agrees in its properties with *p*-benzohydryltetraphenyl methane, must be assigned one of two structures,



The experiments concerning the formation of additive compounds with diphenylnaphthylmethyl lead to results which may seem at first to be wholly unexpected: namely, no addition is found to take place between this compound and the various classes of solvents. Therefore, the commonly accepted view that triphenylmethyl forms additive compounds solely in virtue of its tendency to exist partially in the monomolecular state must be abandoned. For if this were the case we should also have additive compounds with diphenylnaphthylmethyl, and, moreover, to a much greater extent than with triphenylmethyl.

How then can this apparent contradiction be explained? Unquestionably the typical, characteristic reactions of the triarylmethyls, such as oxidation and iodine absorption, are conditioned upon the existence of the equilibrium $R_3C - CR_3 \rightleftarrows 2R_3C$. But it need not necessarily follow that the more the $R_3C$ phase is favored, the greater must be the reactivity of the compound in question. Indeed, on purely *a priori* grounds the very opposite view may be taken with equal force, and this view would apply particularly to such reactions of triarylmethyls as are readily reversible.

Consider for instance the case of triphenylmethyl itself. Hexaphenyl ethane constitutes a system which is on the border line between such ethane compounds wherein the central carbon atoms function as tetravalent and those wherein they function as trivalent. At room temperature the dissociation is only about 2 to 5% at most, but increases on warming and at 80° becomes appreciable, reaching as high as 25 to 30%. Being an unstable system, when chances for the formation of stable irreversible combinations with other compounds are lacking, triphenylmethyl will evidence its unsaturation through temporary, feeble attachment of one radical to another, or through attachment to substances such as ethers, aldehydes, ketones, esters, chloroform, carbon disulfide, and even to completely saturated substances like heptane. But all such combinations, whether it be free radical to free radical or free radical to something else, exist in virtue of the residual, though very feeble, affinity in triphenylmethyl. On the addition to the system of slight amount of energy from outside, as on gentle heating, the union is disrupted and the free radical regenerated. Thus, the obvious predilection of triphenylmethyl to assume the dimolecular state, and its proneness to enter into feeble combination with all possible solvents may be looked upon as consequences of one and the same cause, namely, that the trivalence of the carbon in triphenylmethyl is of a low order of stability. And now consider from the same point of view the case of diphenylnaphthylmethyl. It is monomolecular to the extent of 70% even at 6°; the dissociation increases with the temperature and reaches completion at 60°. Evidently, in this particular free radical the trivalence of carbon is of such high order of stability that the radical lacks the tendency to enter into combination with itself, and presumably for the very same reason it is devoid of tendency to unite with ethers, esters, ketones, etc. Or, if union does occur, it apparently is of such feeble nature that complete dissociation takes place at room temperature. Even in cases where the new compound results from the radical not in virtue of some undefined additional or potential valences but in virtue of definite chemical reaction, the combination may still prove one that is readily reversible, as for instance diphenylnaphthylmethyl iodide, wherein the equilibrium at room temperature is $R_3CI$ 60%, $R_3C$ 40%.

The above considerations lead to this conclusion: the higher the spontaneous dissociation of the hexa-aryl ethane, the greater the comparative stability of the corresponding triarylmethyl is likely to be. It is to be expected that the existence of the monomolecular phase preponderatingly over the dimolecular should be associated with a lack of propensity in the free radical to make additive compounds of the nature which characterize triphenylmethyl. This deduction is derived from the comparison of only two examples, and in the very nature of the case is only tentative. An examination of a large number of free radicals with this end in view is desirable.

It is not intended to convey the impression that the capacity of the hexa-aryl ethanes to form additive compounds is believed to be contingent entirely upon their dissociation. Undoubtedly other factors must be taken into consideration, such as the chemical nature of the individual free radical. Triphenylmethyl forms additive compounds with various solvents for the same reason in part that triphenyl methane itself forms additive compounds with benzene and other solvents. The unsaturation state of triphenylmethyl may greatly enhance its additive properties but it could hardly be considered as the sole factor in the formation of these compounds.

The results of the molecular-weight determinations of diphenylnaphthylmethyl in nitrobenzene, *p*-bromotoluene, *p*-dichlorobenzene, *p*-chlorobromobenzene, and naphthalene prove conclusively that we are dealing here with a phenomenon of molecular dissociation, wherein the products of dissociation are in equilibrium with the dissociating substance. An equilibrium of this nature might be expected to shift in favor of dissociation (1) with dilution, (2) with an increase in temperature.

(1) In every case, regardless of the nature of the solvent, we find that there is a steady increase in the molecular weight as we proceed from a 1% to a 3–4% solution of diphenylnaphthylmethyl, *i. e.*, an increase in concentration shifts the equilibrium in favor of the dimolecular modification and, *vice versa*, a decrease in concentration shifts the equilbrium in favor of the monomolecular modification. Moreover, it is evident from the similarity of the molecular-weight curves, Fig. 1, that this increase in dissociation with dilution is practically independent of the nature of the solvent.

(2) Likewise, we see from Fig. 1 that there is a marked decrease in the molecular weight of diphenylnaphthylmethyl with an increase of temperature, showing that the equilibrium is shifted in favor of dissociation. Indeed, if we compare solutions of a definite concentration, *e. g.*, 2%, and plot the temperatures as abscissas and the corresponding values of the molecular weight as ordinates, we obtain a remarkably smooth curve, shown in Fig. 2. From this curve it is evident that the effect of temperature upon the dissociation becomes greater as we proceed to higher temperatures, for the decrease in molecular weight for a given increase in temperature is not constant but becomes noticeably larger. In other words, between 70 and 80° for example, a change of 1° in the temperature produces a considerably greater effect upon the dissociation than a change of 1° between 10° and 20°.

The smoothness and uniformity of this temperature-molecular weight curve indicates that for a given concentration, the equilibrium between the monomolecular and the dimolecular forms of diphenylnaphthylmethyl is dependent largely upon the temperature and not to any appreciable extent upon the nature of the solvent, for otherwise we should expect noticeable irregularities in the curve.

From Fig. 2 we find that for a 2% concentration the molecular weight of diphenylnaphthylmethyl is approximately 345 at a temperature of 6°; therefore at this temperature an equilibrium is established between 30% of the dimolecular and 70% of the monomolecular form of the free radical. As the temperature is increased, the molecular weight drops until at about 62° it reaches the value of 293, indicating that at this point all of the dimolecular modification has dissociated and only the monomolecular modification is present in the solution.

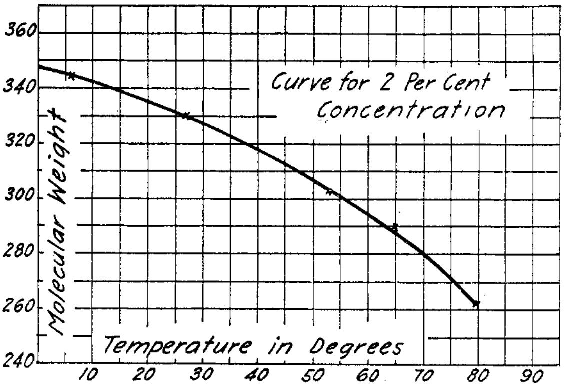


Fig. 2.

The molecular weight however does not become constant above this temperature but continues to decrease, reaching the value of 262 at 80°. And indeed, other free radicals containing naphthyl groups seem to exhibit the same peculiar behavior, as for instance in the case of α-naphthylxanthyl[1] and α-naphthylphenyl(biphenyl)methyl.[2] How can these abnormal values be explained? The possibility arises that under the influence of comparatively high temperatures diphenylnaphthylmethyl may suffer a gradual decomposition of some sort. But any decomposition would necessarily be accompanied by a noticeable variation in the freezing point of the solution, and yet successive determinations showed that, on the contrary, the freezing point remained perfectly constant. Moreover such possibility of decomposition is precluded by the fact that by oxidizing the solution at the end of the experiment, the usual amount of peroxide could be obtained. In a previous contribution dealing with this phenomenon we ventured upon a hazardous explanation, namely that the triarylmethyl may suffer further dissociation with the consequent production of a radical with a bivalent carbon, as for instance:

$$(C_6H_5)_2C - C_{10}H_7 \rightleftarrows (C_6H_5)_2C + C_{10}H_7, \quad \text{or}$$

$$(C_6H_5)_2C - C_{10}H_7 \rightleftarrows (C_6H_5)C(C_{10}H_7) + C_6H_5.$$

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[1] Gomberg and Schoepfle, THIS JOURNAL, 39, 1668 (1917).

[2] Schlenk and Renning, *Ann.*, 394, 195 (1912).

By reducing a solution of the free radical with hydrogen at a temperature of about 100°, and identifying the products formed, it was hoped that it would prove possible to determine whether such a dissociation of the monomolecular diphenylnaphthylmethyl occurs. But as in the case of reduction at ordinary temperatures, the reduced solution contained only diphenylnaphthyl methane so far as the examination revealed. Consequently the explanation suggested above still remains unsupported, and yet it seems difficult to find any other explanation equally satisfactory.

## 5. Summary.

(1) Several new diphenyl-α-naphthylmethyl derivatives have been synthesized and described.

(2) The important chemical reactions of the free radical, diphenyl-α-naphthylmethyl, have been studied including the oxidation, the reduction, the action of iodine, the action of light, and the action of hydrochloric acid.

(3) It has been shown that diphenyl-α-naphthylmethyl, unlike triphenylmethyl, does not form additive compounds with various solvents, in spite of its high degree of dissociation, and a plausible explanation for this difference has been suggested.

(4) By means of a series of exact molecular-weight determinations of diphenyl-α-naphthylmethyl extending over a range of temperature from 6° to 80°, it has been proven that the temperature as well as the concentration has a marked influence upon the degree of dissociation of free radicals, while the nature of the solvent seems to exert but slight influence.

(5) It has been shown that at a temperature of approximately 60° diphenyl-α-naphthylmethyl is present in the monomolecular phase entirely, and that above this temperature the molecular weight suffers a further decrease, the cause of which has not been established.

ANN ARBOR, MICH.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY, No. 323.]

# THE SYNTHESIS OF SOME HOMOLOGS OF THE TERPENES, DERIVATIVES OF 1,4-DIISOPROPYL CYCLOHEXANE.

BY MARSTON TAYLOR BOGERT AND CLARENCE PEAVY HARRIS.[1]

Received July 24, 1919.

## Introductory Part.

An interesting fact concerning the terpenes, and one to which attention often has been called, is that the graphic formulas conventionally assigned

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[1] The investigation reported in this article formed part of the work carried out by Mr. Harris as a candidate for the degree of Ph.D. under the Faculty of Pure Science, Columbia University. Its publication has been delayed by the war duties of the senior author.