readily hydrolyzes it to the amine. When the compound is warmed with sulfuric acid and ethyl alcohol, ethyl benzoate is evolved.

From a hydrosulfite vat it colors cotton and artificial silk a brilliant lemon-yellow, but it shows much less affinity for textile fibres than 1-benzoylamino-anthraquinone, which produces an intense golden yellow.

All efforts to analyze 1-benzoylamino-2-methylanthraquinone by the Dumas combustion method for nitrogen failed. The compound decomposes only at a high temperature, and then does so with almost explosive violence. It was successfully analyzed by the Kjeldahl method, using copper sulfate as a catalyst.

Anal. Subs., 1.9369, 2.3541: 18.00, 21.65 cc. of 0.31036 *N* NaOH. Calcd. for $C_{22}H_{15}O_3N$: N, 4.11. Found: 4.04, 4.00.

Use of 1-Benzoylamino-2-methylanthraquinone as a Vat Dye

The vat was prepared by adding 4 g. of sodium hydrosulfite and 5 cc. of a solution of potassium hydroxide (30 g. per 100 g. of water) to 50 cc. of water; 0.2 g. of 1-benzoylamino-2-methylanthraquinone was added, and the mixture was warmed until the dye had dissolved. A sample of artificial silk (or cotton) weighing 10 g. was then placed in the bath, and the temperature was raised gradually to about 75°. The sample assumed a red-brown color which changed to a lemon-yellow on exposure to the air.

Summary

1. The preparation of 1-benzoylamino-2-methylanthraquinone has been described.

2. Its properties have been compared with those of 1-benzoylamino-anthraquinone.

GAINESVILLE, FLORIDA

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

TRIPHENYLMETHYL. XXXIV. 2,5-, 2,4-, AND 3,4-DIMETHOXY-TRIPHENYLMETHYLS

BY M. GOMBERG AND G. C. FORRESTER[1]

RECEIVED JUNE 1, 1925 PUBLISHED SEPTEMBER 5, 1925

Introduction

It is now well established that a comparatively slight variation in the composition of the aryl groups in hexa-arylethanes may exert a notable influence on the extent of the spontaneous dissociation of these ethanes in solution into free triarylmethyl radicals. It has been found that a methoxyl in the *ortho* position of one of the phenyl groups in triphenylmethyl augments to the extent of 32% the degree to which the free radical exists

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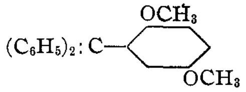
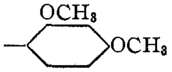
[1] The material here presented is from a dissertation submitted by G. C. Forrester to the Faculty of the University of Michigan in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1923.

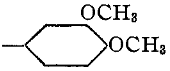
in the monomolecular form.[2] An analogous influence was also observed when the same group was introduced into the *para* position of one of these rings; 30.5% of this free radical exists in the monomolecular form.[3] These facts led us to speculate as to whether two such groups in the same nucleus would exert a proportionately greater influence. It became our intention to prepare the free radicals 2,5-dimethoxy-triphenylmethyl (I), 2,4-dimethoxy-triphenylmethyl (II), and 3,4-dimethoxy-triphenylmethyl (III), and to make a detailed study directing especial attention to their apparent molecular weight, that is, the degree of dissociation of the corresponding hexa-arylethanes.



I



II



III

The happy circumstance that the solutions of the free radicals which we prepared possess considerable color, opened the avenue to further study of the color of free radicals. It became our purpose to investigate further the *quantitative* relations between the changes in concentration of the monomolecular free radical and the changes in color, under different conditions of temperature and dilution in a wide variety of solvents, and to raise anew the question: is the trivalence of carbon the sole cause of color production in these compounds?

Tetraphenylmethane is formed in exceedingly low yield, namely, 2 to 5%, from the action of phenylmagnesium bromide upon triphenylchloromethane. On the other hand, triphenyl carbinol condenses readily with aniline,[4] phenol and anisole,[5] and gives quantitative yields of amino-, hydroxy- and methoxy-tetraphenylmethanes. The increased reactivity which an amino or hydroxyl group imparts to the *para* position of the benzene ring is a recognized fact, and the above-mentioned reactions must, therefore, be attributed to the increased reactivity of the aryl group introduced, rather than to a change in activity of the carbinol or in the space relations of the residues involved. The question arises, is it not possible that methoxyl groups in the carbinol itself may impart to the central carbon atom sufficient activity to effect good yields of tetra-arylmethane?

Discussion of Results

The Triarylmethyls

Free Radicals.—Solutions of the 2,5-dimethoxy-triphenylmethyl bromide, the 2,4-dimethoxy-triphenylmethyl chloride and the 3,4-dimethoxy-

[2] Gomberg and Nishida, This Journal, **45**, 190 (1923).

[3] Gomberg and Buchler, *ibid.*, **45**, 207 (1923).

[4] Ullmann and Münzhuber, *Ber.*, **36**, 404 (1903).

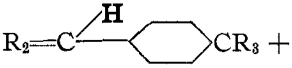
[5] Baeyer and Villiger, *Ber.*, **35**, 3018 (1902).

triphenylmethyl chloride are rapidly converted to solutions of the corresponding free radicals by the abstraction of halogen by the agency of molecular silver.

The free radicals which we crystallized, namely, the 2,5- and the 2,4-methyls, are white, but slowly assume a yellow color with lapse of time even though well protected from light and air. The colors of the solutions in the common organic solvents are various shades of red-orange to pure red. In agreement with previous work, the accumulation of methoxy groups intensifies the red in the color of the solution of triphenylmethyl.

Carefully prepared solutions of the free radicals do not deteriorate with lapse of time. They are also surprisingly stable to heat.

Solutions of these free radicals were very slightly affected by five hours' exposure to strong diffused daylight, and likewise were resistant to the light from a strong tungsten lamp. The direct rays of the sun were necessary to effect a moderately rapid decomposition of the solutions.

Two steps have been observed in the reaction which occurs when free radicals are treated in solution with solvent saturated with hydrogen chloride. They are expressed by the equations, $2R_3C + HCl = R_3CH + R_3CCl$ and $R_3CH + R_3CCl =$  $R_2{=}C\overset{H}{-}\langle\;\rangle CR_3 + HCl$.

Qualitative experiments indicated that our three free radicals react with hydrogen chloride according to the first equation almost exclusively.

Peroxide Formation.—When carefully dried, the radicals absorb oxygen very slowly. However, the rapidity of oxidation in solution is extremely great; in five minutes approximately the calculated quantity of oxygen required for the formation of the peroxide $(R_3C)_2O_2$, is absorbed. The amount of oxygen absorbed frequently varies from that calculated by an amount greater than could be due to experimental error, and on long standing a slow absorption continues to the extent of over 150%. The nature and extent of the side reactions are rather sensitive to prevailing physical conditions, but when these conditions are properly standardized the results obtained are reasonably quantitative. The yields of peroxides were uniformly high, namely, 80 to 97%, and clean crystalline products were obtained.

Reaction with Iodine.—As with free radicals previously studied, the reaction of the addition of iodine to our three free radicals is one of equilibrium.

Dissociation.—Taking the class of hexa-aryl ethanes as a whole, the degree to which the members are dissociated into the monomolecular free radicals is conditioned chiefly by the nature of the aryl groups. The other factors which might affect the degree of dissociation of a given hexa-aryl ethane in solution are the temperature, the concentration of solution and the nature of solvent.

We determined the degree of dissociation of our three free radicals in solutions of various concentrations by an indirect cryoscopic method. The reason for adopting this procedure was that only one, the 2,4-triarylmethyl, could be isolated with sufficient purity to warrant the use of the direct method. A variety of carefully purified solvents was used, their freezing points ranging from 5° to 53°.

As anticipated, increase in temperature augmented appreciably the degree of dissociation in the case of each. Plotting degree of dissociation against temperature, we obtain the accompanying graphic representation of relative change in the former with temperature change (Fig. 1). The nature of solvent, when temperature and concentration are approximately constant, is seen to exert very considerable influence[6] in two cases, the 2,5- and 2,4-dimethoxy compounds, and to be negligible in a third, the 3,4- in benzene and nitrobenzene (Fig. 1). As regards the effect of concentration, little if any positive influence is observable.

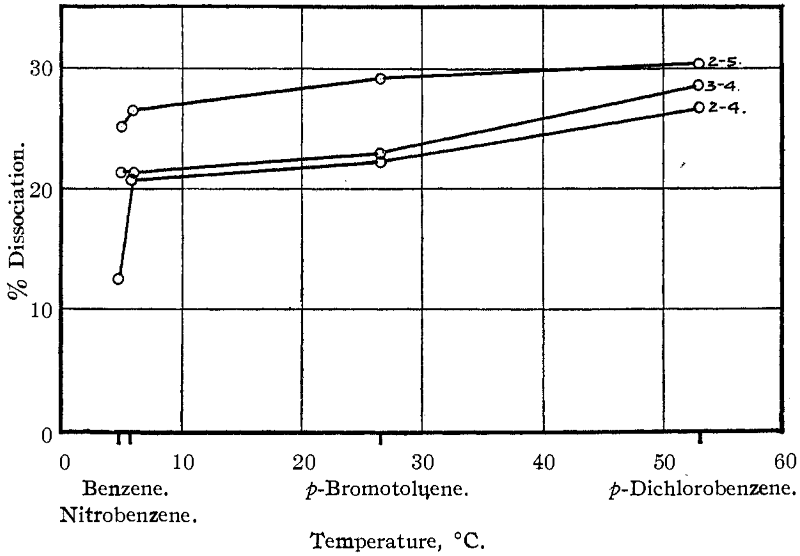


Fig. 1.—Variations of percentage dissociation of the three hexa-arylethanes with the temperature.

Contrary to expectations based on findings with the monomethoxytriphenylmethyls, we found that the presence of two methoxy groups in the same nucleus alters but slightly the ratio of monomolecular free radical to the hexa-arylethane. The variation in the orientation as we changed from the 2,5- to the 2,4- and then to the 3,4-methyl is accompanied by no very striking change in results. Perhaps we should have been prepared for this last observation, since the two monomethoxy-triphenylmethyls

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[6] Gomberg and Sullivan, This Journal, **44**, 1810 (1922).

mentioned, the *ortho* and *para*, have about the same degree of dissociation. In a subsequent paper it will be shown that distribution of the methoxy group in separate phenyl nuclei has by far greater effect than the accumulation of the same number in one nucleus. Radicals monomolecular to the extent of 90–100% are thus obtainable.

Color of Free Radicals

The technical aspect of the work with the color of the solutions of free radicals resolved itself into color intensity comparison. The change in depth of color due to concentration or temperature change was followed by altering the height of a second column of standard reference solution of the same material until the same depth of color was obtained. The intensity of the first was read as proportional to the height of this second column.[6] This standard or reference solution used was always a solution of the same free radical in the same solvent as the solution under examination. In this work the standard solution was 1% concentration. The other solutions ranged from 1 to 5% and perfect matches in quality of color were readily obtained.

Change in temperature frequently shifts the position of the absorption bands and breaks them up, that is, affects the color of the solution.[7] Although in one phase of the work the temperature of the solutions examined ranged from 50° below that of the standard to as high as 50° above, no difficulty was observed in matching the quality of the changing color by simply varying the height of the standard. Needless to say, the work was carried on with adequate precautions against injurious effects of light and with rigorous exclusion of oxygen, all solvents having been boiled to free them from dissolved air before use.

That changes in the solution which resulted in change in color intensity were time reactions, was evident at particularly low temperatures. This was preëminently observable in the singular case in which increase in color followed the lowering of the temperature below a certain minimum (Fig. 6). However, maintenance at these temperatures for ten minutes sufficed to attain equilibrium such that even another hour's treatment brought no further change in color intensity. In all other cases, equilibrium shifted very rapidly with changing temperature and the first reading we took did not differ from that taken after an hour's maintenance of the system at that constant temperature.

Results on Dilution.—From the results of the molecular-weight experiments by direct and indirect methods with all three free radicals, we found that concentration over a range of 1 to 5% had little effect on the extent to which dissociation of the hexa-arylethane proceeds. However, dilution in the color comparator from 5% concentration to 1% in the case

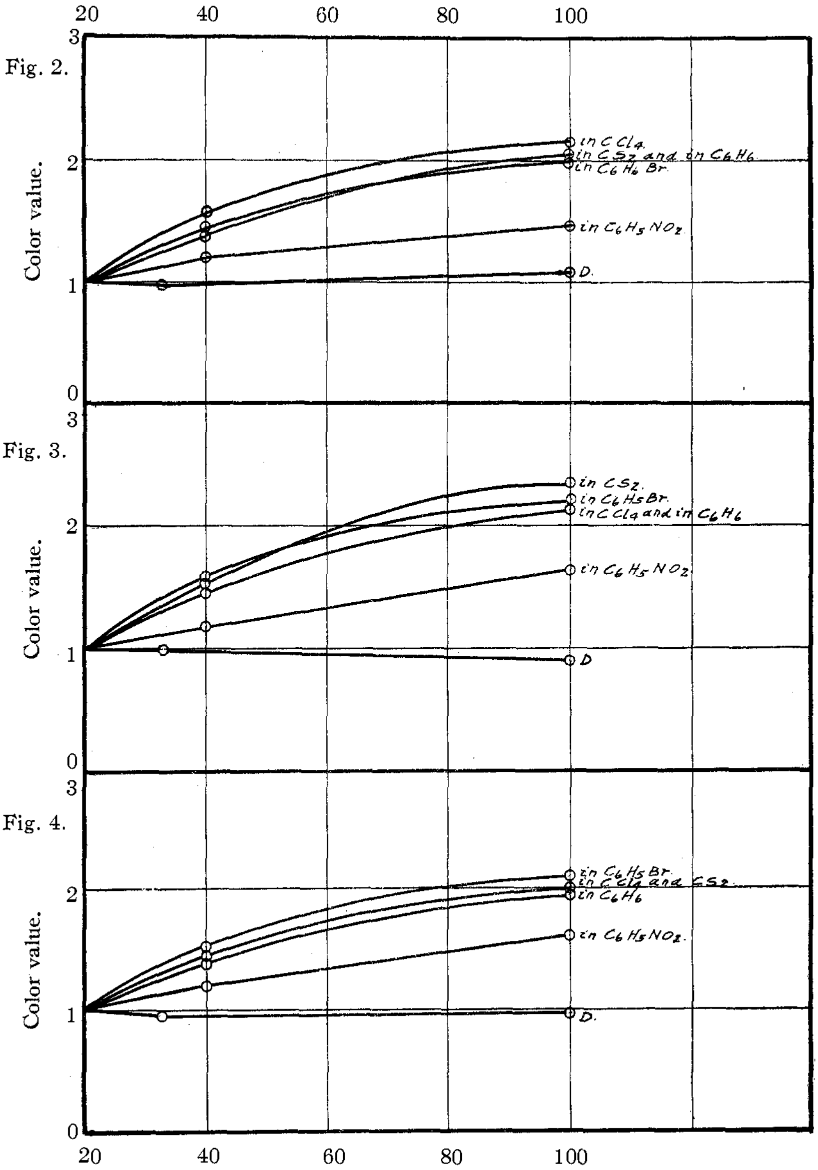
[7] Wood, "Physical Optics," The Macmillan Co., **1921**, p. 441.

of each free radical, in each of several solvents, approximately doubles the intensity of color, with the single exception of nitrobenzene solutions, which case we shall treat presently. Plotting the color values against

Fig. 2.

Fig. 3.

Fig. 4.



Figs. 2, 3 and 4.—Variations in color values of the dimethoxy-triphenylmethyls with dilution. Curves D, dissociation value.

dilution we obtain the accompanying curves, Figs. 2, 3 and 4, showing the relative change in intensity of color accompanying dilution. The color value of the solution of 5% concentration is taken as unity and that of the other dilutions calculated in terms of this by reference to the height of column. Similarly, taking the percentage dissociation of the hexa-aryl ethane at 5% concentration as unity and calculating the relative degree of dissociation at other dilutions, we obtain, by plotting these values against dilution, Curves D (Figs. 2, 3 and 4). They show a relative absence of change in degree of dissociation with dilution.

Were color of free radicals due specifically to the formation of the monomolecular triarylmethyl, then conversely a change in degree of dissociation must not only accompany but must parallel color change. It does neither. The facts observed, on the other hand, are in no way contradictory to the assumption that color is due to a quinonoid tautomer of the monomolecular triarylmethyl, since the fact that tautomeric equilibrium may shift with varying concentration, has the support of experiment.[8] Further, the unique behavior of nitrobenzene solutions (Figs. 2, 3 and 4) favors our hypothesis. These solutions already highly colored, that is, highly tautomerized, at 5% concentration cannot undergo relatively as much further quinoidation, and consequently with increased dilution the equilibrium cannot be so greatly shifted toward the colored form.

Results with Change of Temperature.—It was found that solutions of the free radicals in bromobenzene and in toluene were almost colorless at —30°, with one exception. This was the case of the 2,4-dimethoxy free radical in bromobenzene, Fig. 6, to be discussed later. Increase in temperature caused the color to deepen rapidly. Plotting the color values against the temperature we obtain the curves in Figs. 5, 6 and 7. These show the relative change in intensity of color accompanying changing temperature.

To show graphically how unrelated the color values are to the amount of monomolecular free radical at the same temperatures, we have constructed Figs. 8, 9 and 10. We took the amount of monomolecular radical at 4.9° as our unit and calculated the relative amounts at other temperatures with reference to this unit. Plotting these values against the temperature, we obtained Curves Y showing increase of dissociation of the ethane with rise of temperature. Similarly, we took the color intensity at 4.9° as unity and calculated the relative color intensity at other temperatures. We then plotted these values against the temperature and obtained Curves A and B, showing increase in color intensity with rise in temperature. We see that from 5° to 53° the dissociation of the hexa-arylethane increased only 30%, 40% and a little over 100% in the maximum case. On the other

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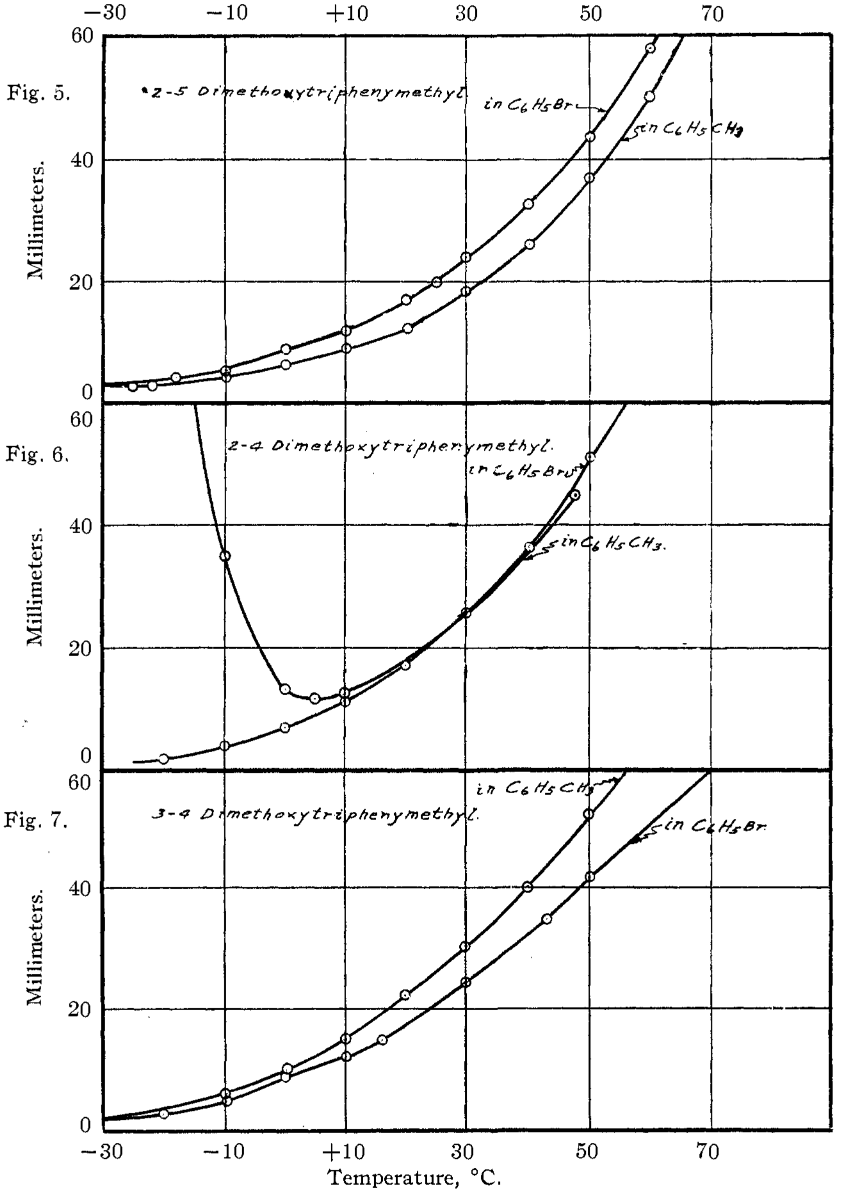
[8] Wislicenus, *Ann.*, **291**, 147 (1896). Meyer and Kappelmeier, *Ber.*, **44**, 2722 (1911). Miller, *J. Russ. Phys.-Chem. Soc.*, **47**, 1544 (1915).

hand, the color increase over this range of temperature averaged well over 400%, showing a minimum of 400% and a maximum of over 600%. Again, change in the degree of dissociation does not parallel color change.



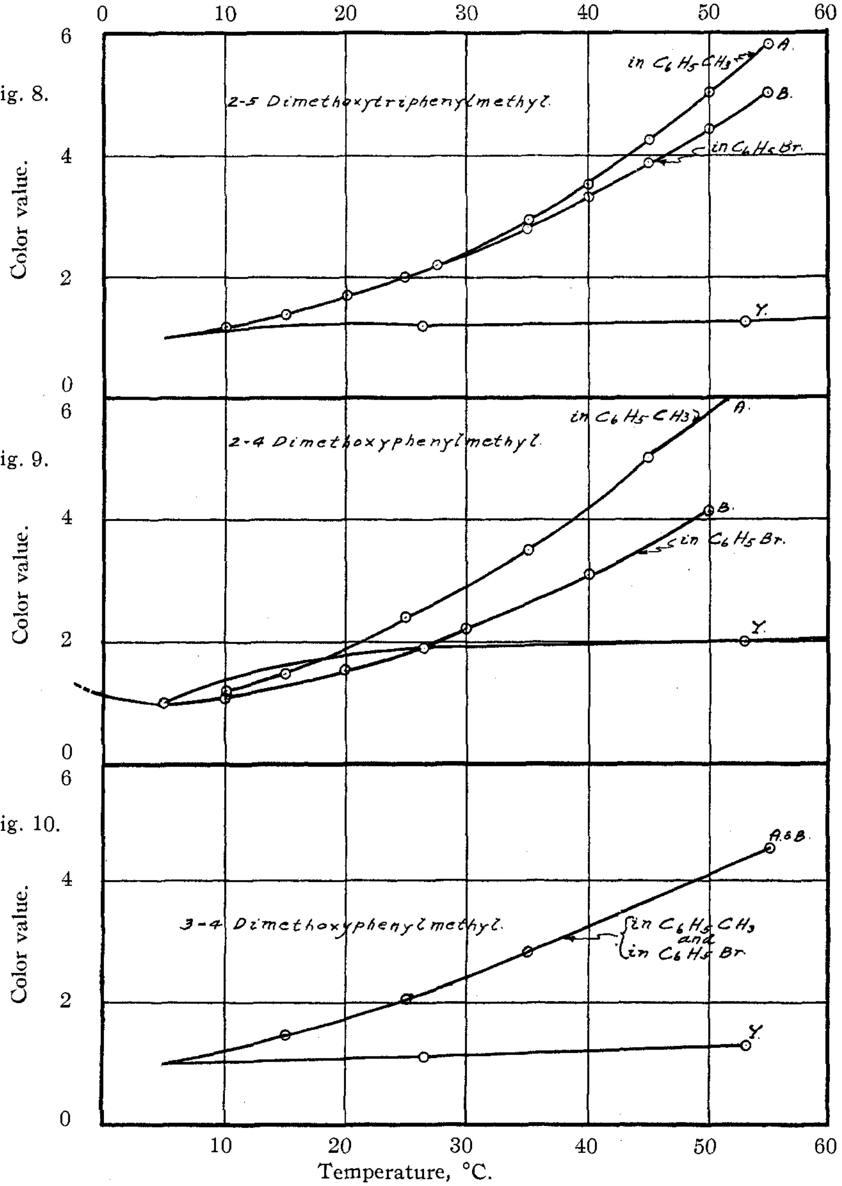
Figs. 5, 6 and 7.—Variations in color of the dimethoxy-triphenylmethyls with the temperature.

We are at present at a loss to know how to explain the unexpected and apparently anomalous portion of the color-intensity curve for the 2,4-free radical between +5° and —25° (Figs. 6 and 9).

Fig. 8.

Fig. 9.

Fig. 10.



Figs. 8, 9 and 10.—Relation of variation in color of the solution of radicals with temperature to variation in amount of the monomolecular form present. A and B are color curves; Y, dissociation curves.

Methoxy-Substituted Tetra-arylmethanes

For the tetra-arylmethane syntheses, a standard method of reacting the triarylmethyl halide with the Grignard reagent was adopted. $R_3C\underline{Cl} + C_6H_5Mg\underline{Br} = R_3C.C_6H_5 + MgBrCl$.

We chose phenylmagnesium bromide as our standard reagent for introducing the fourth aryl group in nearly all cases of preparing the tetra compounds. From numerous experiments in this Laboratory and elsewhere, we may take the ability to give a 5–10% yield of tetra compound as a unit wherewith to measure the reactivity of the triphenyl carbinol carbon atom as compared to that in other triaryl carbinols when brought into reaction with the same Grignard reagent under like conditions.

We found that mono-*o*-methoxy-triphenyl carbinol chloride yielded the corresponding tetra compound in excess of 38%, whereas mono-*p*-methoxy-triphenyl carbinol chloride yielded but 4.3% of the calculated quantity. The 3,4-dimethoxy-triphenyl carbinol chloride gave a yield of 30% of tetra compound while the 2,5- chloride gave the highest yield, 58%. This was duplicated, using the bromide instead of the chloride. The 2,5- chloride was treated with magnesium-α-bromonaphthalene and 41% of the corresponding tetra compound was obtained. In spite of precedent[9] we now treated the 2,5- bromide with phenylmagnesium iodide and were rewarded by a 17% yield of the sought-for product.

In the case of the 2,4- tetra compound, we found that 25% of the calculated yield may be obtained. However, in certain instances the Grignard reagent in this reaction acted as a reducing agent, and instead of the tetra compound we obtained the triarylmethane in yield up to 53%. Similar reducing effects, with apparently contradictory results, have been observed before.[10]

In the case of each of the dimethoxy-tetra compounds, attempts were made to prepare them from the corresponding phenol-dimethyl ethers and triphenylchloromethane. $(C_6H_5)_3C.Cl + (CH_3O)_2{:}C_6H_3.MgI = (C_6H_5)_3{:}C.C_6H_3(CH_3O)_2 + MgICl$. In no case were we successful, although the arylmagnesium bromides, as well as the iodides, were used.

Experimental Part

2,5-Dimethoxy-triphenylmethyl

Preparation of the 2,5-Dimethoxy-triphenyl Carbinol.—This carbinol was first synthesized by Kauffmann and Grombach,[11] from 2,5-dimethoxy-

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[9] Schmidlin, *Ber.*, **43**, 1137 (1910). Schroeter, *Ber.*, **36**, 3005 (1903). Zelinsky, *Ber.*, **35**, 2692 (1902).

[10] Franzen and Diebel, *Ber.*, **38**, 2716 (1905). Busch and Fleischmann, *Ber.*, **43**, 740 (1910). Letellier, *Compt. rend.*, **146**, 343 (1908). Hess and Rheinboldt, *Ber.*, **54**, 2043 (1921). Meisenheimer, *Ann.*, **442**, 180 (1925).

[11] Kauffmann and Grombach, *Ber.*, **38**, 800, 2703 (1905).

benzophenone and phenylmagnesium bromide. However, a method based on the action of benzophenone dichloride with hydroquinone-dimethyl ether in the presence of anhydrous aluminum chloride gives equally good yields and uses materials more easily procured.

In 40 cc. of carbon disulfide was dissolved 13.8 g. of hydroquinone-dimethyl ether prepared according to Ullmann,[12] and to the solution was added 23.9 g. of benzophenone dichloride. To this solution, well stirred, was added 13.5 g. of anhydrous aluminum chloride in small portions during the course of an hour. When addition was complete the temperature of the mixture was slowly raised to the boiling point of the solvent. Upon decomposition of the aluminum chloride double salt with ice, the carbinol was usually obtained as a cleanly crystalline compound, especially so when washed with warm 5% sodium hydroxide solution. One recrystallization from benzene or alcohol gave a pure white, crystalline product melting sharply at the recorded temperature of 141°; yield, 92%.

Kauffmann describes 2,5-dimethoxy-triphenylmethyl chloride as being easily prepared by passing dry hydrogen chloride into a benzene solution of the carbinol in the presence of anhydrous sodium sulfate. We failed to prepare the chloride with the calculated chlorine content (calcd. 10.48%; found, 9.0 to 9.5%) and of the recorded melting point, 98°. We therefore resorted to the use of the carbinol bromide instead of the chloride in all further work.

2,5-Dimethoxy-triphenylmethyl Bromide, $[(CH_3O)_2C_6H_3]\ (C_6H_5)_2CBr$.—Thirty-two g. of the carbinol was dissolved in 50 cc. of benzene, and a 5% excess of acetyl bromide was added to the solution which was then warmed on the water-bath for an hour. The solution was concentrated at 40° under reduced pressure to the appearance of crystals, then well cooled, an equal volume of petroleum ether added and the mixture filtered in the absence of moisture. To remove traces of acid, the product was recrystallized from warm benzene and petroleum ether and dried in a desiccator over soda-lime and paraffin; m. p., 113°.

Anal. Calcd. for $C_{21}H_{19}O_2Br$: Br, 20.87. Found: 20.78, 20.94.

2,5-DIMETHOXY-TRIPHENYLMETHYL ANILIDE is very soluble in chloroform and benzene, less soluble in ethyl acetate, ether and ethyl alcohol. After recrystallization from ethyl acetate or alcohol it melts at 169.5°.

2,5-DIMETHOXY-TRIPHENYLMETHYL-*p*-TOLUIDE melts at 151°.

Preparation of the 2,5-Dimethoxy-triphenylmethyl.—Oxygen-absorption methods furnished us with a convenient means of studying the progress of the reaction of molecular silver with the carbinol halides used, and of measuring the stabilities of the resulting free radicals.

Sealed tubes containing 0.7 g. of the bromide and 0.7 g. of very pure molecular silver suspended in carefully dried bromobenzene were prepared. After a three-hour period of shaking, one such solution absorbed 102.1% of the calculated amount of oxygen and after a 24-hour period another absorbed 99.5%.

Other tubes similarly prepared were subjected for two and one-half hours to temperatures of 66° and 80°. Upon testing their quality, we found that they absorbed 102.0 and 95.6% of the calculated amount of oxygen, respectively.

Five per cent. solutions of the free radical in thin quartz test-tubes were exposed to light of different degrees of intensity. One exposed for five hours to strong diffused daylight still absorbed 93.8% of the calculated quantity of oxygen. Another exposed for five

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[12] Ullmann, *Ann.*, **327**, 116 (1903).

hours to the direct rays of a 60-watt tungsten lamp at a distance of 25 cm. absorbed 88.0% and a third exposed for seven hours to bright sunlight still absorbed 52.3% of the calculated amount.

To a benzene solution containing 1 g. of the free radical was added 10 cc. of ether saturated with dry hydrogen chloride. The color characteristic of the free radical disappeared completely in five minutes and the solution assumed the green color distinctive of the solution of the 2,5-carbinol chloride in the presence of hydrogen chloride.

The radical can be obtained in crystalline state. Two hours' shaking with 5 g. of silver was found to suffice for complete removal of the bromine from a 5g. sample of the bromide. The bright red solution was siphoned into the apparatus previously described and concentrated until its volume had been reduced to 8 or 10 cc. An equal volume of petroleum ether (25–40°) was added. For purposes of experiment, only the first crop of crystals, which amounted to about 50% of the calculated yield, was used. The product was a white, crystalline powder, quite stable in air when well dried, but which invariably acquired a light yellow color on standing for a short time. However, after many days, even in an atmosphere of nitrogen or carbon dioxide, the compound lost its crystalline form and changed into a gummy, red mass no longer capable of absorbing oxygen.

We found that it was impossible to free the crystals completely from solvent without effecting decomposition of the free radical, even when the drying was conducted under diminished pressure. The drying material darkened in color and tended to cake into a brittle mass. It lost in weight from 5 to 10%, but the residue absorbed even less oxygen than prior to being dried.

The vapors evolved in the drying process, upon examination by combustion, proved to consist of both carbon disulfide and petroleum ether. The presence of these solvents rendered it impossible to obtain by the direct cryoscopic method reliable molecular weights of the free radical.

THE 2,5-DIMETHOXY-TRIPHENYLMETHYL PEROXIDE, $[(CH_3O)_2C_6H_3.(C_6H_5)_2C]_2O_2$.—This was prepared from a solution of 2,5-dimethoxy-triphenylmethyl exposed to air. Upon recrystallization from benzene it gave a melting point of 149°. The peroxide is soluble in chloroform, slightly soluble in benzene, alcohol, carbon tetrachloride and carbon disulfide, but quite insoluble in the other common organic solvents. It is decomposed in hot solution, almost 50% being changed when its benzene solution is boiled for five minutes.

Anal. Calcd. for $C_{42}H_{38}O_6$: C, 78.96; H, 6.00. Found: C, 78.41; H, 6.06.

IODINE FACTOR.—Two per cent. solutions of the free radical in carbon disulfide were titrated, in an atmosphere of carbon dioxide, with 0.1 *N* iodine solution, and also in carbon disulfide. We found, on two trials, that equilibrium was reached when 54.6 and 51.7% of the calculated amount of iodine had been added. The presence of R_3CI was demonstrated by converting it to the anilide, which product upon isolation proved to be identical with the anilide prepared from the corresponding bromide.

2,4-Dimethoxy-triphenylmethyl

Preparation of the 2,4-Dimethoxy-triphenylmethyl Carbinol.—This carbinol had previously been prepared by Kauffmann and Pannwitz,[13] from the 2,4-dimethoxy-benzophenone. Here, too, as in the case of the 2,5-dimethoxy-triphenyl carbinol, we found a more convenient and economical method in its preparation from benzophenone dichloride and resorcinol-dimethyl ether through the use of a Friedel and Crafts reaction. The

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[13] Kauffmann and Pannwitz, *Ber.*, **45**, 773 (1912).

identity of the carbinol thus obtained was confirmed by the melting point and reduction to the methane.

2,4-Dimethoxy-triphenylmethyl Chloride.—The ease with which this compound forms a red addition product with hydrogen chloride rendered its preparation, by use of the latter as a halogenating agent, inconvenient. However, acetyl chloride diluted with petroleum ether was used for this purpose with good results. The product which crystallized was washed by decantation with petroleum ether and the powdered mass dried in a vacuum over soda lime and paraffin; yield, 95%. When carefully protected from moisture the crystals remained white indefinitely, but when exposed occasionally to the air of the laboratory they turned pink and then dark red; m. p., 97°.

Anal. Calcd. for $C_{21}H_{19}O_2Cl$: Cl, 10.48. Found: 10.43, 10.47.

When the chloride was exposed to a slow current of dry hydrogen chloride, it immediately turned red and in a few hours changed to a sticky mass with an increase in weight corresponding to more than two molecular equivalents of hydrogen chloride. This product, placed in a vacuum desiccator over soda lime, resumed the crystalline form and appearance of the chloride.

2,4-DIMETHOXY-TRIPHENYLMETHYL ANILIDE is recrystallized best from ethyl acetate, which yields fine, white crystals; m. p., 143°.

Preparation of 2,4-Dimethoxy-triphenylmethyl.—This free radical, tested for stability in the same manner as described for the 2,5 free radical, gave an absorption of oxygen of 101.9%, after a lapse of three hours in solution and 98.0% after a 24-hour period. The resistivity to heat was also tested as before. A solution kept at 66° for two and one-half hours still absorbed 101.2% of oxygen, and one subjected to 80° for a like period of time absorbed 104.2%. Exposure to light as previously described resulted as follows: 81.7% absorption after five hours in strong diffused daylight; 97.2% absorption after five hours at a distance of 25 cm. from a 60-watt tungsten lamp; and only 6.0% after seven hours in bright sunlight. This solution was almost colorless while the two former were not visibly affected.

Hydrogen chloride destroyed this free radical also, although the color change required two hours to become complete.

The procedure that was most successful in the preparation of 2,5-dimethoxy-triphenylmethyl was also found to be the best of many tried in attempting to isolate this triarylmethyl. Because of somewhat lower solubility, this free radical has a greater tendency to separate as an oil. Hence, the mother liquor in which the crystals form must contain a higher concentration of the solvent carbon disulfide. The product, after drying for one hour in a vacuum at room temperature, absorbed oxygen in agreement with the calculated amount. By further drying the free radical in the Abderhalden apparatus, a loss in weight was noted varying from 2.7 to 4.0%. This free radical showed comparatively great stability to the drying process, which had very little effect on the oxygen absorption of the product.

The 2,4-DIMETHOXY-TRIPHENYLMETHYL PEROXIDE was prepared in the same manner as was the 2,5 isomer. When recrystallized from benzene it melted at 146°. Boiling alcohol effects a slow decomposition of the peroxide, while boiling benzene decomposes it quite rapidly.

Anal. Calcd. for $C_{42}H_{38}O_6$: C, 78.96; H, 6.00. Found: C, 78.70; H, 5.95.

IODINE FACTOR.—As with the 2,5- isomer, this free radical was examined to determine its iodine factor. Two experiments yielded the values 40.6 and 43.2%.

3,4-Dimethoxy-triphenylmethyl

Preparation of the 3,4-Dimethoxy-triphenylmethyl Carbinol.—This carbinol had been previously prepared by Sachs and Thonet[14] from 3,4-dimethoxy-benzophenone and phenylmagnesium bromide. We found a more convenient method in its preparation from benzophenone dichloride and catechol dimethyl ether through Friedel and Crafts' reaction.

3,4 - Dimethoxy - triphenylmethyl.—3,4 - Dimethoxy - triphenylmethyl chloride has been described by Sachs and Thonet.[14] We have not yet isolated the corresponding triarylmethyl in crystalline form but the fact that we had it in solution was attested by the absorption of oxygen in the calculated amount with the formation of the peroxide. When the peroxide was recrystallized from benzene or carbon tetrachloride it melted at 162.5°.

Anal. Calcd. for $C_{42}H_{38}O_6$: C, 78.96; H, 6.00. Found: C, 78.89; H, 5.93.

The oxygen absorption of a solution of this free radical, that had been prepared three hours earlier, was 107.4%; and of one that had stood for 24 hours was 106.7%.

A solution of this free radical held at a temperature of 66° for two and one-half hours absorbed 103.5% of oxygen, and one held at 80° for a like period of time absorbed 108.1%.

Solutions exposed to light in the manner previously described gave the following results: 99.5% absorption after five hours' exposure to strong, diffused daylight; 97.2% after five hours' exposure at a distance of 25 cm. from a 60-watt tungsten lamp; and 17.9% after seven hours in bright sunlight. The last solution was almost colorless, and the other two were not visibly affected.

Hydrogen chloride also changed this free radical, and considerable quantities of the 3,4-methoxy-triphenyl carbinol chloride and 3,4-methane were isolated.

IODINE FACTOR.—Two experiments yielded the values 55.9 and 58.4%.

Dissociation of the Tetramethoxy-hexaphenylethanes

Having concluded that we could not isolate each of the three radicals free from solvent of crystallization and of such purity as determination of molecular weights would demand, we decided to use an indirect method of obtaining the desired data.[15]

We used the customary freezing-point tube with side arm, equipped with a Beckmann thermometer and a two-ring platinum electromagnetic stirrer, the halide and silver being contained in the side arm and introduced at will into the solvent. The whole operation was conducted in an atmosphere of nitrogen. With the weight of the solvent determined, its freezing point was noted. When solution of the halide was complete, the new freezing point was taken. Then the silver was introduced into the solu-

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[14] Sachs and Thonet, *Ber.*, **37**, 3332 (1904).

[15] Gomberg and Cone, *Ber.*, **37**, 2040 (1904). Lecher and Goebel, *Ber.*, **54**, 2223 (1921). Gomberg, THIS JOURNAL, **45**, 415 (1923).

tion in small quantities. Stirring was continued in the meanwhile for an hour, while the solution was protected from the light, and the new freezing point was then found. The quantity of silver halide was determined immediately after the necessary readings had been taken, as a check on the completeness of the reaction. The quantity found was always in excess of 96% of that calculated.

The constant *K* for each solvent was determined under the same conditions that prevailed in the molecular-weight determinations of the free radicals. For this work triphenylmethane and benzophenone, both carefully purified by repeated vacuum distillation and recrystallization, were used.

The fortunate fact that in 2,4-dimethoxy-triphenylmethyl we had a free radical which we could prepare and isolate in a high degree of purity and that therefore we could feel safe in the determination of its degree of dissociation by the direct method as well as by the indirect, enabled us to test further the efficacy of the indirect method.

From our results we found that in benzene at concentrations between 1 and 7% an average of seven determinations gave a molecular weight of

TABLE I

THE MOLECULAR WEIGHT OF DI-DIMETHOXY-HEXAPHENYLETHANES DETERMINED BY THE INDIRECT METHOD

Solvent	F. p. °C.	Concn. %	Depress. by Halide	Depress. after silver	Concn. of free radical	Devian. %	Dissocn. %
		1. DI-2,4-DIMETHOXY-HEXAPHENYLETHANE					
Benzene	4.9	3.6+	0.571	0.319	3.3	—0.75	11.9
		3.6—	.536	.304	3.2	+ .75	13.4
Nitrobenzene	5.8	3.28	.678	.406	2.8	— .90	19.8
		3.16	.668	.406	2.8	+ .90	21.6
p-Bromotoluene	26.6	2.82	.717	.431	2.5	—2.05	20.1
		2.75	.702	.436	2.5	+2.05	24.2
p-Dichlorobenzene	53.0	3.12	.738	.468	2.8		26.8
		2. DI-3,4-DIMETHOXY-HEXAPHENYLETHANE					
Benzene	4.9	1.0—	.156	.096	0.9	+0.6	23.1
		4.02	.637	.390	3.6	+ .1	22.6
		4.21	.670	.403	3.8	—2.2	20.3
		4.41	.710	.440	4.4	+1.5	24.0
Nitrobenzene	5.8	2.97	.630	.382	2.7	0.0	21.3
		3.18	.683	.414	2.8	0.0	21.3
p-Bromotoluene	26.6	2.65	.664	.406	2.4	— .7	22.3
		2.72	.684	.423	2.4	+ .7	23.7
p-Dichlorobenzene	53.0	3.15	.742	.477	2.9		28.6
		3. DI-2,5-DIMETHOXY-HEXAPHENYLETHANE					
Benzene	4.9	0.98	.137	.086	.9	+1.75	27.0
		3.82	.532	.327	3.0	—2.35	22.9
		3.79	.530	.334	3.0	+0.75	26.0
		5.30	.732	.458	5.0	—0.15	25.1
Nitrobenzene	5.8	3.06	.567	.374	2.4	+1.8	28.3
		2.99	.558	.348	2.4	—1.8	24.7
p-Bromotoluene	26.6	2.7	.600	.384	2.2	+0.5	29.7
		3.0—	.648	.417	2.3	— .5	28.7
p-Dichlorobenzene	53.0	2.95	.617	.399	2.3	— .85	29.5
		3.03	.634	.416	2.4	+ .85	31.2

537.1, with an average deviation from the mean of ±4.7, corresponding to a dissociation of 12.8%, with an average deviation from the mean of 1.0%. In *p*-bromotoluene, concentrations between 1 and 2% with five determinations gave an average molecular weight of 508.2, with an average deviation from the mean of ±6.3, corresponding to a dissociation of 19.3%, with an average deviation from the mean of 1.5%. Five determinations in *p*-dichlorobenzene in concentrations between 1 and 3% gave an average molecular weight of 475.6, with an average deviation from the mean of ±7.1, corresponding to a dissociation of 27.4%, with an average deviation from the mean of 1.9%.

Color Study

The colorimeter for the study of intensity of color of the solution of the free radicals was that described by Gomberg and Sullivan.[6]

The Effect of Dilution.—This work was carried on at an approximately constant room temperature. A known volume of 5% solution was compared with the 1% standard and the mean of several readings taken. The solution was then diluted to 2.5% strength by the addition of an equal volume of the proper solvent and again compared with the standard. Finally it was diluted to 1% strength and the height of standard necessary to match the resulting color measured. Table II is a sample of the data obtained, from which were plotted the curves of Figs. 2, 3 and 4.

Table II

Effect of Dilution

Solvent Vol.	Concn.	CS_2	CS_2	CS_2	C_6H_5Br	C_6H_5Br	$C_6H_5NO_2$	$C_6H_5NO_2$
		Height of column in standard in mm.					Corrected	
Initial	5%	14.0	14.0	14.0	16.0	16.0	20.5	20.5
1st dilution	2.5%	19.5	19.5	19.0	22.5	22.0	25.5	24.5
2nd dilution	1%	29.0	29.5	28.0	33.0	32.0	29.5	29.5
Temperature, °C.		23	23	23	23	23	24	24

With nitrobenzene as a solvent, it is obvious that on dilution we are adding the color of the additional solvent over and above that of the free radical. The correction for this was determined in the following manner. A solution of azobenzene which approximated the color of the free radical in nitrobenzene was prepared in one tube of the colorimeter B. A reference solution of one-fifth this strength was prepared in the reservoir connected with the second tube A, of the colorimeter. Dilution in B should cause no change in the level in A necessary to balance B if the solvent were colorless and the solute such that Beer's law applied, as is the case with azobenzene. The additional height necessary in A is a measure of the added color effect in B due to the additional solvent. Thus a correction of 2.5 mm. for 2.5% dilution of our free radicals and 4.5 mm. for 1% dilution at the volumes with which we worked was found and applied to the corresponding readings in nitrobenzene, solutions, giving us the nitrobenzene "corrected" readings.

The Effect of Temperature.—The solution under examination and the standard were prepared as before, although a larger volume of standard was usually necessary. The solution in B after preliminary cooling in ice and salt was further cooled in a mixture of toluene and solid carbon dioxide and quickly replaced in the frame of the colorimeter. By means of a thermometer having a short bulb, sealed within Tube B, the changing temperature of the solution was read. Readings of the standard necessary to balance the color of the solution were taken in rapid succession and simultaneously the temperature of the solution was noted. The standard was at the temperature of the room which remained constant within a degree throughout the experiments. The usual procedure was to take a series of readings from —30° to +10° two or three times and then slowly raise the temperature to a maximum which preliminary experiment had shown to be in keeping with safety. Two or more series of readings were taken from this maximum down to room temperature and, to assure ourselves that no harmful effects had been produced by the high temperatures attained, readings were again taken from —30° up to room temperature. This series always duplicated those taken first. At the lowest temperatures attained some color still persisted and absolutely colorless solutions were never obtained. The data obtained are contained in Figs. 5, 6 and 7; the average deviation of duplicate readings was ±1 mm. From these figures Curves A and B in Figs. 8, 9 and 10 were plotted.

Tetra-arylmethanes

2,5-Dimethoxy-tetraphenylmethane $[(CH_3O)_2C_6H_3]\ (C_6H_5)_3C$.—(a) To phenylmagnesium bromide in ether solution was added dropwise one-third of a molecular equivalent (7.66 g.) of 2,5-dimethoxy-triphenylmethyl bromide in benzene solution. This operation consumed an hour and was carried on in an atmosphere of hydrogen and at the temperature of boiling ether, which was maintained for several hours longer. Then the contents of the flask were treated with acidulated water and steam distilled. After the mixture had cooled, the water was poured off from the hardened mass, the latter was dried, dissolved in benzene, the solution concentrated and the tetra compound crystallized by addition of petroleum ether. A yield of 4.4 g. of the substance, or 58%, was obtained; m. p., 163°. The compound can be recrystallized from alcohol or ether, but best from acetic acid.

Anal. Calcd. for $C_{27}H_{24}O_2$: C, 85.22; H, 6.36. Found: C, 85.07; H, 6.36.
Mol. wt. Calcd.: 380. Found: 373.1, 373.4, 372.3, 372.6.

(b) To phenylmagnesium iodide was added 7.66 g. (one-third of a molecular equivalent) of 2,5-carbinol bromide; 1.28 g. of 2,5-tetra-arylmethane, representing a yield of 17%, was obtained after unusually troublesome purification.

(c) To phenylmagnesium bromide was added 9.35 g. (one third of a molecular equivalent) of 2,5-carbinol chloride; 6.1 g. of 2,5-tetra compound was readily obtained; yield, 58%.

(d) Efforts to obtain the tetra compound by (1) condensing the 2,5-carbinol with benzene by means of phosphorus pentoxide, (2) condensing triphenyl carbinol with hydroquinone-dimethyl ether by means of phosphorus pentoxide, and (3) triphenylchloromethane with both the dimethyl ethers of hydroquinone-magnesium bromide[16] and iodide, all met with failure.

2,5-Dimethoxy-triphenyl-α-naphthylmethane, $[(CH_3O)_2C_6H_3](C_6H_5)_2C.(C_{10}H_7)$.—To α-naphthylmagnesium bromide was added 6.77 g. (one-third of a molecular equivalent) of 2,5-carbinol chloride; 3.53 g., representing a 41% yield, of 2,5-dimethoxy-triphenyl-α-naphthylmethane was obtained. The substance crystallizes best from acetic acid; m. p., 175°.

Anal. Calcd. for $C_{31}H_{26}O_2$: C, 86.47; H, 6.09. Found: C, 86.28; H, 6.26.

Mol. wt. Calcd.: 430. Found: 407.4, 403.6, 410.1; av., 407.

3,4-Dimethoxy-tetraphenylmethane.—(a) To phenylmagnesium bromide was added 6.77 g. (one-third of a molecular equivalent) of 3,4-carbinol chloride; 2.34 g. of the tetra compound was recovered; yield, 30%. It crystallizes best from glacial acetic acid; m. p., 170.5°.

Anal. Calcd. for $C_{27}H_{24}O_2$: C, 85.22; H, 6.36. Found: C, 85.20; H, 6.34.

Mol. wt. Calcd.: 380. Found: 370, 368.8, 368.0.

(b) To the dimethyl ether of catechylmagnesium iodide[17] was added 5.54 g. (one-third of a molecular equivalent) of triphenylchloromethane. No tetra-aryl compound was obtained.

2,4-Dimethoxy-tetraphenylmethane.—(a) To phenylmagnesium bromide, was added 6.77 g. (one-third of a molecular equivalent) of 2,4-carbinol chloride; 3.2 g. of the dimethoxy-triphenylmethane, m. p. 124°, was obtained; yield, 52.6%.

Anal. Calcd. for the methane $C_{21}H_{20}O_2$: C, 82.86; H, 6.62. Found: C, 82.90, 82.72, 82.71; H, 6.56, 6.47, 6.53.

Mol. wt. Calcd.: 304. Found: (I) 299.5, 301.8, 302.6; (II) 304.6, 302.9.

(b) Another attempt to prepare this tetra-aryl compound was made using 6.77 g. of the chloride and three molecular equivalents of phenylmagnesium bromide. This trial succeeded with a 25% yield. The product, recrystallized several times from acetic acid in which it is but partly soluble even when hot, melts at 180° and gives no appreciable color with concd. sulfuric acid.

Anal. Calcd. for $C_{27}H_{24}O_2$: C, 85.22; H, 6.34. Found: C, 84.96; H, 6.23.

Mol. wt. Calcd.: 380. Found: 382.7, 371.0.

(c) To the dimethyl ether of resorcinolmagnesium iodide,[18] was added 5.54 g. (one-third of a molecular equivalent) of triphenylchloromethane. No tetra-aryl compound nor methane was isolated.

Mono-*o*-methoxy-tetraphenylmethane $[(CH_3O)C_6H_4](C_6H_5)_3C$.—To phenylmagnesium bromide was added 6.16 g. (one-third of a molecular equivalent) of mono-*o*-methoxy-triphenylmethyl chloride; 2.67 g. of the tetra-aryl compound was isolated; yield, 38%. Recrystallized from glacial acetic, it melts at 145°.

Anal. Calcd. for $C_{26}H_{22}O$: C, 89.10; H, 6.33. Found: C, 88.80; H, 6.4.

Mol. wt. Calcd.: 350. Found: 343.9, 349.7, 351.4.

Mono-*p*-methoxy-tetraphenylmethane.—To phenylmagnesium bromide was added 3.9 g. (one-third molecular equivalent) of mono-*p*-methoxytriphenylmethyl chloride; 0.185 g. of the tetra-aryl compound was obtained; yield, about 4.5%. Recrystallized from acetic acid, it melts[6] at 194°.

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[16] Noelting and Werner, *Ber.*, **23**, 3250 (1890).

[17] Seer and Karl, *Monatsh.*, **34**, 647 (1913).

[18] Kauffmann and Kieser, *Ber.*, **45**, 2334 (1912).

Anal. Calcd. for $C_{26}H_{22}O$: C, 89.10; H, 6.33. Found: C, 89.16; H, 6.39.
Mol. wt. Calcd.: 350. Found: 345.0, 346.3, 346.6.

Summary

1. A number of derivatives of 2,5-dimethoxy-, 2,4-dimethoxy- and 3,4-dimethoxy-triphenyl carbinol have been synthesized.

2. The free radicals, 2,5-dimethoxy- and 2,4-dimethoxy-triphenylmethyl, have been isolated. A detailed study of the chemical properties of these and of 3,4-dimethoxy-triphenylmethyl has been made. The degrees of dissociation of the three hexa-arylethanes have been determined over a range of temperature from 5° to 53°, and over a concentration range of from 1 to 6%. The degree of dissociation was found to be influence by temperature and nature of solvent and but little affected by concentration of the solution. The 2,5- compound dissociates from 24 to 32%, the 2,4- compound from 12 to 27% and the 3,4- compound from 21 to 29%.

3. Studies were made of the effect of dilution and of temperature on the color of several solutions of the free radicals. It was found that dilution augmented the intensity of color considerably, but the amount of monomolecular free radical changed an inappreciable amount. It was found that a change in temperature from 5° to 53° caused the intensity of the color to increases not less than 400% in any case, and yet a corresponding change in temperature increased the amount of monomolecular free radical but slightly over 100% in the maximum case. We conclude that while color formation in solutions of the hexa-arylethanes may be concomitant with dissociation, it is *not* due specifically to the triarylmethyl form as such. On the other hand, a distortion in molecular configuration of these, such as is implied in the theory of quinonoid forms, to which color is attributed, in equilibrium with the benzonoid is entirely in harmony with the results obtained.

4. Certain mono- and dimethoxy-tetra-arylmethanes were synthesized with especial regard to yield of product as related to orientation of the methoxy groups. The facts observed are not in harmony with the assumptions of steric hindrance.

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