

ORGANIC RADICALS¹

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I. INTRODUCTION

Definition of radical. The concept of "radicals," originally introduced by Lavoisier and later developed more fully by Berzelius, Dumas, Liebig, and then again by Bunsen, Kolbe, Frankland and others, implied that in the molecules of an organic substance there is at least one immutable cluster of atoms which remains undestroyed throughout all the chemical transformations of that substance. Radicals were thus assumed to play the very same function in the organic as the elements do in the inorganic compounds; accordingly, the elements were considered as simple radicals, while the radicals in the organic compounds were "compound radicals." The strife waged long and bitter as to what particular cluster of atoms is to be considered as the radical in any given group of related substances, and also whether radicals are merely creations of our own subjective thinking, figments of our imagination, or whether they have, or may acquire, an independent existence. Finally, with the general acceptance in 1858-1860 of the theory of valence of the elements, and of the theory concerning the structure of the molecules as based on the valence of atoms, the concept of "radical" came to cover any group of atoms which remains unchanged in the molecule of the substance that has undergone a chemical reaction. After the universal concurrence in the belief that carbon, in distinction from many other elements, possesses an unvarying valence, namely that of four, the concept of radical has acquired a new and more specific meaning: by the term was designated usually a portion of the molecule

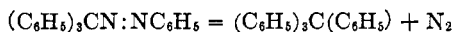
¹ An essay prepared in connection with the dedication of the Sterling Chemistry Laboratory.

wherein, if separated from the rest of the molecule, there would be one carbon atom functioning in a state of valence not normal to it, that is less than four. Obviously, granting the constancy of the valence of carbon, the independent existence of free radicals becomes a contradiction and is inconceivable. Thus, after 1865, the interest in the existence of free radicals became dormant, except for such sporadic speculations as those of Butlerow and of Von Laar, who tried to account for the phenomenon of tautomerism by assuming that the molecules of a substance dissociate into radicals which then recombine so as to form new molecules of a constitution different from the former.

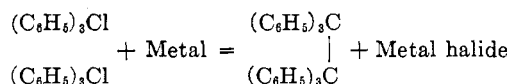
The brilliant experimental work of Nef, 1890–1900, focussed anew the attention of chemists to the question, does carbon always function as tetravalent? Is it not divalent in many other compounds as well as it is in carbon monoxide? He succeeded in marshalling a formidable array of facts in favor of his view, especially in favor of the view that carbon is divalent in the isonitriles. While such an explanation fits in admirably with all the manifold behavior of these substances, it could not, however, be denied that a consistent explanation based upon the quadrivalence of carbon may serve equally well. We had in the views of Nef a revival of the old discussion as to the constitution of the so called unsaturated compounds, and which ended, in 1871, in the general acceptance of the theory of double and triple bonds. The new factor of Nef's queries was,—must we assume that carbon functions in its maximum valence also in those unsaturated compounds where the unsaturation in the molecule is centered not on two adjoining carbon atoms, but on a carbon and a nitrogen atom in union with each other? The question, are isonitriles $R - N \equiv C$ or $R - N = C$, is like an echo of the old question,—is acetylene $H - C \equiv C - H$ or is it $H - C - C - H$? Nef was so successful in adducing evidence in favor of the divalent nature of carbon in the isonitriles, that, notwithstanding the feasibility of another and a less radical explanation, his views have found acceptance in many authoritative texts.

The old question, therefore whether carbon in any of its organic compounds ever possesses a valence of less than four,—has received through Nef's work a renewed interest.

Tetraphenylmethane. From the time when Kekule and Franchimont, in 1872, first prepared triphenylmethane attempts to prepare the analogous hydrocarbon tetraphenylmethane were made by Hemilian, Fridel and Crafts, E. and O. Fischer, Magati, Schwatz, V. Meyer, Weisse, Waga, and Meisel, but the results were seemingly without success. In 1897 the writer described a hydrocarbon which was prepared by heating triphenylmethaneazobenzene and which was supposed to be tetraphenylmethane:



The reaction was more complex in reality than is indicated in the equation, and the yield of the hydrocarbon was exceedingly small, from 2 to 5 per cent. Consequently it seemed desirable to make a comparative study of the physical and chemical characteristics on some similar completely phenylated hydrocarbon as for instance on hexaphenylethane, proceeding on the supposition that it would prove easier to obtain large amounts of the latter than of tetraphenylmethane. The contemplated method for this preparation was one in accordance with the following general reaction:



Hexaphenylethane, triphenylmethyl.

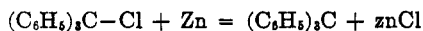
Accordingly, triphenylbromomethane in benzene was treated with metallic sodium but without success. The chloro compound gave no better results. Molecular silver was substituted for sodium. After several hours' boiling a white crystalline body began to separate, and on filtering the hot benzene solution a considerable amount of the same substance separated on cooling. It was recrystallized from benzene, gave a constant melting point, 185°C., and contained no halogen. In its high melting point and in its only slight solubility in the usual

organic solvents it resembled closely tetraphenylmethane, and this new body was taken for hexaphenylethane. An elementary analysis gave, however, the following results:

	Calculated for (C ₆ H ₅) ₃ C ₂	Found
Carbon.....	93.83	87.93
Hydrogen.....	6.17	6.04

. . . Several new lots of the same substance were made both from the triphenylbromomethane and triphenylchloromethane, and purified by successive recrystallization from benzene, chloroform, acetic ether, and carbon disulphide. They all gave the same results entirely concordant with each other. . . . I therefore came to the conclusion that the body under consideration was not a simple hydrocarbon, but an oxygen derivative. The oxygen could come from either of two sources: first, the molecular silver may have contained some oxide of the metal; second, the atmospheric oxygen may act upon the hydrocarbon. I next proved that it is really the oxygen from the atmosphere which oxidizes the hydrocarbon. . . . By working in an atmosphere of carbon dioxide no such insoluble compound is produced, even on weeks' and months' treatment of the halogen bodies with silver, mercury or zinc in benzene. . . . The compound formed is extremely unsaturated. A solution of it in benzene or carbon disulphide absorbs oxygen with great avidity and gives an insoluble oxygen compound. It absorbs chlorine, bromine and iodine. . . .

The experimental evidence presented above forces me to the conclusion that we have to deal here with a free radical, triphenylmethyl, (C₆H₅)₃ ≡ C. On this assumption alone do the results described above become intelligible and receive an adequate explanation. The action of zinc results, as it seems to me, in a mere abstraction of the halogen, leaving the free radical,



The radical so formed is apparently stable, for it can be kept both in solution and in the dry crystalline state for weeks. The radical refuses to unite with another one of its kind, and thus forms a distinct exception to all similar reactions. . . .

The existence of triphenylmethyl implies, of course, the existence of *trivalent carbon*, at least in this particular instance. The conception of such a trivalent carbon in this instance is entirely distinct from that which is ascribed to it by some in benzene, or even in ethylene, where

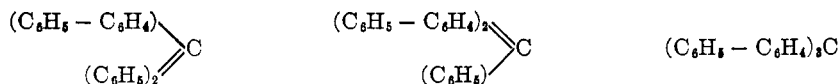
there are always two adjoining carbon atoms acting as trivalent. The unsaturation in such cases has always been indicated by a "double linking." In triphenylmethyl there is *only one carbon atom* that is unsaturated. The existence of such a body means that when three valences of carbon are taken up by three phenyl groups it is difficult, or perhaps even impossible, to introduce as a fourth group such a complicated radical as $(C_6H_5)_3C-$. Only simpler groups, chlorine, bromine, iodine, oxygen, etc., may still combine with such a carbon atom. Whether this be due to the negative character of the three phenyl groups, or whether it is caused by the fact that these groups take up so much space around the carbon atom as to hinder the introduction of another complicated group, is a question of an entirely different nature and need not be discussed here. There are, however, numerous reactions which go to show that there is a limit to the number of complicated groups which can ordinarily be linked to one and the same carbon atom. . . . Now, as a result of the removal of halogen from triphenylchloromethane the fourth valence of the methane carbon is bound either to take up the complicated group $(C_6H_5)_3C-$ or remain as such, with carbon as trivalent. Apparently the latter is what happens (1).

Objection to the theory of trivalent carbon. Following the publication of the above paper a detailed study of the striking and unusual behavior of triphenylmethyl was made by various investigators. It was also demonstrated that this hydrocarbon is but an example of a large class of similar *triarylmethyl* compounds. However for almost ten years the existence of these free radicals still remained a question of dispute. On the chemical side, the evidence in favor of the trivalency of carbon seemed convincing; and yet, the molecular weight of the hydrocarbon in various solvents indicated that it possessed the composition $[(C_6H_5)_3C]_2$, as if it were after all, hexaphenylethane.

Thus, the argument which had proven so decisive in eliminating from the realm of free radicals even those outstanding historical examples—the cyanogen of Gay Lussac, the cacodyl of Bunsen and the alkyls of Frankland and Kolbe—this very same argument was now being invoked against the triarylmethyls. The latter also were all inferred to be dimolecular, for such at least appeared to be the case with triphenylmethyl itself. True, at $80^\circ C.$, in naphthalene as the solvent, the molecular weight of

triphenylmethyl was found to be much less than dimolecular, 415 instead of 486. The conclusion was drawn even at that early time, first, that at this temperature measurable dissociation must be occurring into monomolecular triphenylmethylys; second, this phenomenon of dissociation, be it ever so slight at room temperature, furnishes a satisfactory explanation of the unsaturated behavior of the compound, since we may assume that there exists a dynamic equilibrium between hexaphenylethane and triphenylmethyl.

Acceptance of the theory. At the present time, it seems strange that the examination of the molecular state of the other triarylmethyls, aside from triphenylmethyl, was delayed for so long a period after the discovery of triphenylmethyl. Had this been done early, it would have been recognized at once that triphenylmethyl, as regards its dimolecular phase, is an exception to rather than a typical example of the class of triarylmethyls. Soon after Schlenk reported, in 1910, that the three triarylmethyls of the composition:



exist as monomolecular to the extent of 15, 80, and 100 per cent respectively, many other triarylmethyls were also found to be monomolecular to a large degree. Moreover, a reexamination of the original data obtained on triphenylmethyl itself, was now interpreted anew as indicating that it, too, is monomolecular at room temperature to the extent of 5 to 17 per cent. Thus, the one seemingly valid argument, in fact, the only objection that was at any time raised against the constitution of the triarylmethyls as free radicals, turned out on closer examination to be but a phantom argument.

With the establishment of the actual existence of free triarylmethyls containing a carbon atom in the abnormal, or rather unnormal, state of valence, the search was extended to a study of the behavior of other elements in this respect. We now speak of radicals which contain divalent and tetravalent nitrogen, or

monovalent oxygen, or trivalent lead, trivalent tin, and the field is still being extended.

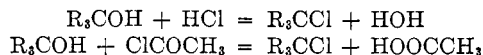
In the following pages an attempt will be made to sketch retrospectively some of the important features of this new chapter of organic chemistry. The group of compounds which contain a trivalent carbon will be described quite fully, and the compounds with other elements in abnormal state of valence will be described in lesser detail.

II. COMPOUNDS WHICH CONTAIN TRIVALENT CARBON

1. *Triarylmethyls and analogs*

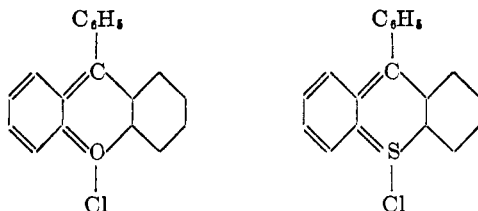
Preparation. During the first few years the work on free radicals was limited almost exclusively to the triarylmethyls wherein each aryl group was linked independently and directly to the central methane carbon atom. Subsequently, analogs of triphenylmethyl were prepared, namely, derivatives of anthraquinone, xanthone, thioxanthone, and acridine.

No important changes have been introduced into the process of preparing triarylmethyls as originally described, although new and interesting methods of formation of these radicals have been discovered. From the laboratory point of view, not infrequently the most difficult part is the preparation of the requisite triarylcbinols, especially those with complex aryl groups. The conversion of the carbinols into the corresponding carbinol chlorides has become much simplified since it has been shown by the writer that the former react readily, when dissolved in benzene or in ether, with hydrogen chloride or with acetyl chloride in this manner:



In the xanthone series the problem proved more complex. Here the arylxanthenyl and thioxanthenyl chlorides, which should correspond to the triarylmethyl chloride, were assumed as non-

existent; instead, isomeric colored chlorides of the constitution involving tetravalent oxygen or sulfur were described:



It was found that this misconception rested on insufficient and erroneously interpreted experimental evidence. By the use of more exact methods colorless carbinol chlorides were prepared which proved to be entirely analogous to the triarylmethyl chlorides, except that they were somewhat less stable than the latter. The same is true in a modified sense, of the acridine series.

For the abstraction of halogen from the carbinol halide, one still depends upon silver, zinc or mercury; but finely divided copper, in the form of copper bronze, has also been suggested by Schlenk and used with success. Unfortunately copper requires for reaction a somewhat higher temperature than the other metals do, and many radicals suffer decomposition when heated for long periods; moreover, a large excess of the metal has to be employed. Taking all circumstances into account, molecular silver seems to us to be the most suitable metal; it takes out the halogen quite readily at room temperature, it need not be in large excess over the calculated amount, it is compact and thus very little of the solution containing the free radical is retained by the metal.

The choice of solvents is very wide: benzene, ether, carbon disulfide, acetone, ethyl acetate, petroleum ether, have all been used. The choice is governed primarily by the relative solubility of the free radical in the particular solvent, and also by the ease with which the solvent may be rapidly concentrated or removed without injury to the radical.

Generally speaking, the essential conditions for the preparation of free radicals are: (1) exclusion of all moisture in order

to prevent partial hydrolysis of the carbinol halide; (2) absence of oxygen; (3) avoiding exposure of the solutions to direct sunlight, since light induces inter-molecular oxidation and reduction of the radicals; (4) avoiding even traces of acids. Schmidlin, Schlenk, and the writer have each described some form of apparatus which meets all the above requirements.

The general procedure in our laboratory as now in use, is as follows: Three to ten grams of the carbinol chloride is placed in a tube of suitable size, of shape *A*, figure 1. From 2 to 3 times the calculated amount of molecular silver is introduced, the tube is almost completely filled with the solvent, and stoppered with a well fitting cork which carries on its under surface a cap of parchment paper. The tube is now placed on a shaking machine for several hours. With very finely divided silver, the reaction may be completed in thirty to forty-five minutes. The liquid is then siphoned over from the tube *A* into bulb *B* and is either concentrated under reduced pressure or is removed completely and then replaced by a different solvent, as the case may be. Upon cooling the concentrated solution, the triarylmethyl usually crystallizes out. The liquid is drawn off, by suction, through the stopcock *C* and the crystalline material is washed and dried in the bulb, with the pump still in action while a slow stream of carbon dioxide is passed through. The yield of the pure crystalline substance will vary, but is usually from 50 to 80 per cent of the calculated, depending upon the solubility of the substance in the solvent from which it crystallized. In the preparation of acridyl radicals, a somewhat modified procedure is necessary, but this need not be discussed here.

A large number of triarylmethyls, about 65, have been prepared and definitely characterized through their oxidation into the corresponding peroxides; of these about 20 radicals have been isolated in the solid state for purposes of molecular weight determination, but only about 6 have been carefully studied with the same detail as triphenylmethyl has been.

Stability. While triphenylmethyl itself, in the solid state, is quite stable and may be kept undecomposed for several years, other triarylmethyls differ very widely as regards stability.

Some have been found to retain their unsaturated character only a few hours, and others become isomerized or decomposed by the time their solution is concentrated to dryness. Appar-

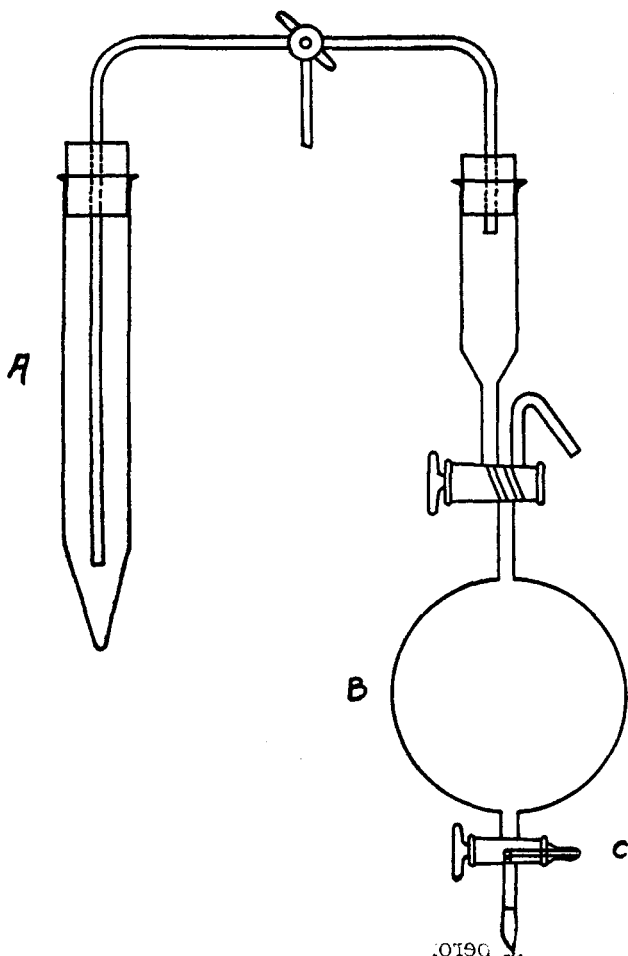


FIG. 1

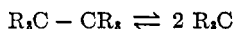
ently radicals which contain in the nucleus the groups, OH, OCH₃, OCH₂, C₆H₅, OCOCH₃, NO₂, are among the least stable.

Color of the radicals in the solid state and in solution. Most of the radicals that have been isolated so far, are colorless or

so nearly colorless in the solid state as to make it appear probable that the yellow coloration has been occasioned by slight oxidation of the substance on the surface of the crystals. In solution, however, each shows its own characteristic selective absorption, solutions of every color of the spectrum have been described, from yellow through orange, red, green to deep violet. The complexity of the aryl groups is not the only factor that determines the intensity of the color. Generally speaking, naphthyl groups give greater depth of color; α -naphthyldiphenylmethyl gives a deep reddish brown solution, while the analogous β -naphthyl radical gives a solution of pure red color. Again, while di-*p*-chlorotriphenylmethyl gives an orange yellow solution, *o-p'*-dichlorotriphenylmethyl gives violet-red, and the di-*o*-chlorotriphenylmethyl gives a deep violet solution. Methyl groups intensify the color from yellow towards orange; methoxy groups, more towards red. Interesting is the influence of nitro groups: *p*-nitrotriphenylmethyl gives an intensely green solution, not unlike that of malachite green, while tri-*p*-nitrophenylmethyl gives a solution which can easily be mistaken for that of fuchsine. The radicals of the type $\langle \text{C}_6\text{H}_4 \rangle \text{C-R}$ are all colorless in the solid phase, and also when in solution. On being heated the solutions assume a deep blue fluorescence, and at a still higher temperature the solutions become brown. With cooling, the change is reversible. The xanthenyl radicals give solutions of deeper and more intense color than those of the triaryl methyls.

From the fact that the triarylmethyls are almost colorless when solid and become intensely colored when dissolved, we must conclude that, in dissolving they undergo a change in molecular structure. To Schmidlin belongs the credit for having established by experiment that, even in solution, both modifications, the colorless and the colored, exist in equilibrium with each other. He showed that when triphenylmethyl is first dissolved the solution remains colorless for a few seconds, then begins to turn yellow and very soon reaches a permanent intensity. If now air is allowed to come in contact with this

solution a small amount of peroxide is produced and the color is discharged, only to reappear again in a few seconds. This can be repeated several times. The number of such successive decolorizations indicates, it is generally assumed, the relative proportions of the two modifications of the free radical. This phenomenon has been explained by the assumption that the colorless radical is hexa-arylethane, the colored is the free radical proper:



The inadequacy of this explanation will be discussed later in the paper.

Conductivity. Triarylmethyl chlorides, and especially the bromides, when dissolved in liquid sulfur dioxide, as has been shown by Walden and also by the writer, or in liquid hydrocyanic acid (2), behave like true salts; they conduct the electric current to a degree equal to that of ethylamine hydrochloride, and the molecular conductivity increases with the dilution. We must therefore consider the triarylmethyl chlorides as "carbonium" salts, which dissociate into R_3C^+ and Cl^- . But how shall we interpret the remarkable fact that triarylmethyls, in liquid sulfur dioxide, also conduct the current? Do we have two kinds of ions, R_3C^+ and R_3C^- , which correspond to two kinds of monomolecular triarylmethyls, or does the loose compound formed from the solute and solvent dissociate into ions: $((R_3C)_2 - SO_2) = 2 R_3C^+ + (SO_2)^-$? The question must be left open for the present.

It should be mentioned that the absorption spectrum of triphenylmethyl in benzene is different from that in sulfur dioxide; also the absorption spectrum of triphenylmethyl radical is different from that of the triphenylmethyl ion which is produced by dissolving the carbinol in sulfuric acid.

Molecular weight. This has been determined for a number of free radicals with most painstaking care, as this constant is the final and the decisive criterion as to what extent the substance is in the monomolecular state, i.e., to what extent it is actually a free radical. The cryoscopic method, for the most

part, has been used with quite a variety of solvents freezing at temperatures of -22 to $+80^{\circ}\text{C}$. The per cent of dissociation of the hexa-arylethane into the free radicals has been calculated from the formula

$$X = \frac{M_t - M_o}{M_o} \times 100$$

where M_o is the molecular weight calculated from the depression of the freezing point, and M_t is that corresponding to the calculated for the hexa-arylethane under examination.

In our laboratory, the determinations were always made on freshly prepared samples, the concentrations of the solute being from 1 to 5 per cent. We have aimed to get appreciable depression of the freezing point of the solvent, from 0.200° to nearly a degree. In this way we hoped to eliminate, to some extent, the errors inherent in the method.

In table 1 are summarized the results obtained in the molecular weight determinations of a number of hexa-arylethanes. Only those data have been incorporate in this table which were obtained at moderately low temperatures, with benzene or nitrobenzene at 5°C ., and *p*-bromotoluene at 27°C ., as the solvents. The ethanes are arranged in order of their approximate complexity. Such a table permits ready comparison of the various hexa-arylethanes with respect to their tendency towards dissociation, since under these conditions the effects of temperature and solvent may be disregarded.

Factors influencing degree of dissociation of hexa-arylethanes. The principal factor is, the nature of the aryl groups; also, for the same hexa-arylethane the degree of dissociation must also depend upon the nature of the solvent, the concentration of the solute and the temperature at which the observation is made.

It is clear from the table that we may have hexa-arylethanes of all possible gradations of dissociation, the differences in the degree depending upon the nature of the aryl groups. Our knowledge concerning this influence is still too meager to permit of sweeping generalizations. Only such results can be of use in these comparisons which have been obtained on different

TABLE 1

	SOLVENT	CONCENTRATION		DISSOCIATION		OBSERVER
		From per cent	To per cent	From per cent	To per cent	
1. Hexaphenylethane	{ Benzene <i>p</i> -Bromotoluene	2.3		None		Gomberg
		3.2		Sl. assoc.		
2. Di-(<i>o</i> -methoxy)-hexa-phenylethane	{ Benzene <i>p</i> -Bromotoluene	5.2	1.7	22.9	29.5	Gomberg and Nishida
		2.7	0.81	30.8	33.4	
3. Di-(<i>p</i> -methoxy)-hexa-phenylethane	{ Benzene <i>p</i> -Bromotoluene	6.27	1.47	22.1	27.1	Gomberg and Buchler
		4.75	1.21	30.2	31.3	
4. Di-(<i>p</i> -benzyloxy)-hexa-phenylethane	{ Benzene <i>p</i> -Bromotoluene	4.53	1.17	26.7	42.4	Gomberg and Buchler
		5.16	1.17	25.6	39.9	
5. Di-(2-4 methoxy)-hexa-phenylethane	{ Benzene <i>p</i> -Bromotoluene	6.5	1.8	12.9	12.0	Gomberg and Forrester
		2.7		20.1		
6. Di-(3-4 methoxy)-hexa-phenylethane	{ Benzene <i>p</i> -Bromotoluene	4.0		22.6		Gomberg and Forrester
		2.6		23.7		
7. Di-(2-5 methoxy)-hexa-phenylethane	{ Benzene <i>p</i> -Bromotoluene	4.0		22.9		Gomberg and Forrester
		2.6		29.7		
8. Di- α -naphthyl tetra-phenylethane	{ Nitrobenzene <i>p</i> -Bromotoluene	2.71	0.90	68.0	78.6	Gomberg and Schoepfle
		2.96	0.89	73.5	91.5	
9. Di- β -naphthyl tetra-phenylethane	{ Benzene <i>p</i> -Bromotoluene	6.42	1.72	27.2	32.3	Gomberg and Sullivan
		5.53	1.76	27.7	30.6	

10. Di-biphenyl tetra-phenylethane	Benzene	2-3	15.0		Schlenk
11. Tetra-biphenyl di-phenylethane	Benzene	1.82	79.0	0.78	Schlenk
12. Hexa-biphenylethane	Benzene	3.44	100.0	1.45	Schlenk
13. Di-biphenyl di-naphthyl diphenylethane	Benzene	3.16	120.0	1.27	Schlenk
14. Di-biphenylene di-phenylethane	Benzene	0.58	None		Schlenk
15. Phenyl anthronyl	Benzene	1.49	33.6	1.22	Schlenk
16. 2-2' sulfonido-triphenylmethyl	Benzene	2.96	22.0	0.98	Gomberg and
	<i>p</i> -Bromotoluene	3.12	22.0	0.90	Britton

arylethanes under nearly the same experimental conditions as to solvent and the concentration of the solute. A comparison in table 1 of hexa-phenylethane with the *o*- and *p*-methoxy- and *p*-benzyloxy-derivatives brings out the influence of the oxygen in the nucleus of the aryl groups in enhancing the dissociation tendencies of hexa-phenylethanes. And yet, judging from results soon to be published, two methoxy groups on the same nucleus do not seem to have any more influence than a single group. The successive substitution of the three phenyl groups by the heavier biphenyl groups leads to arylethanes with progressively increasing dissociation tendencies, i.e., 15, 80 and 100 per cent.

In order to get further information on this question, Gomberg and Schoepfle (3) made careful molecular weight determinations on a selected series of hexa-arylethanes, all the determinations being made in the same solvent, namely, in naphthalene, at 80°C. The following seven substances were used:

1. $(C_6H_5)_3C$ triphenylmethyl
2. $(C_6H_5)_2C.C_{10}H_7$ α -naphthyl-diphenylmethyl
3. $C_6H_5.C \begin{array}{l} \diagup C_6H_4 \\ \diagdown C_6H_4 \end{array} O$ phenyl-xanthyl
4. $CH_3C_6H_4.C \begin{array}{l} \diagup C_6H_4 \\ \diagdown C_6H_4 \end{array} O$ *p*-tolyl-xanthyl
5. $ClC_6H_4.C \begin{array}{l} \diagup C_6H_4 \\ \diagdown C_6H_4 \end{array} O$ *p*-chlorophenyl-xanthyl
6. $C_{10}H_7.C \begin{array}{l} \diagup C_6H_4 \\ \diagdown C_6H_4 \end{array} O$ α -naphthyl-xanthyl
7. $C_6H_5.C \begin{array}{l} \diagup C_6H_4 \\ \diagdown C_{10}H_6 \end{array} O$ phenyl-pheno- β -naphtho-xanthyl

The results which were obtained are summarized in figure 2.

From Schlenk's results with biphenyl-hexa-arylethanes one might infer that the dissociation of the hexa-arylethane into free radicals is greatly favored by the complexity or the weight of the aryl groups, the dissociation becoming apparently more

manifest also in proportion to the number of such groups. Some support in favor of this inference is given by the α -naphthyl-diphenylmethyl, which was found to be monomolecular to the

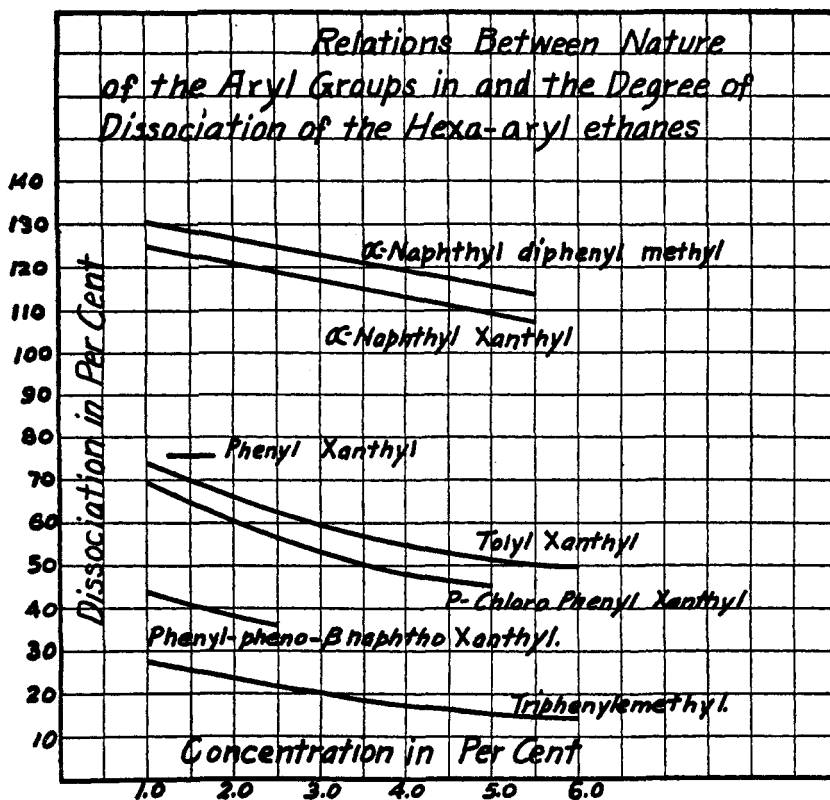
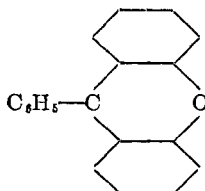
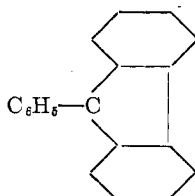


FIG. 2

extent of 60 per cent. But the hypothesis that the dissociation of the hexa-arylethanes is proportional to the complexity of the aryl groups becomes wholly untenable when one compares triphenylmethyl with phenyl-xanthyl,



which is monomolecular to the extent of 75 per cent. Is the union of the two phenyl groups the paramount influence in this case? If so, why should a substance, constitutionally so closely related to the xanthyls as phenyl-biphenylene-methyl is,



be completely dimolecular? Again, an α -naphthyl group when replacing a phenyl group in triphenylmethyl exerts upon the dissociation equilibrium of the compound a very decided influence in favor of the monomolecular phase, α -naphthyldiphenylmethyl appearing as wholly dissociated. This favorable influence of the naphthyl group is still retained when the group is linked to a xanthone ring, the resulting compound being also dissociated to the extent of 100 per cent. And yet, when the naphthyl group enters as a component in the formation of the xanthone ring itself, it depresses very decidedly the dissociation tendency of the compound, as is evident on comparing the two isomers, α -naphthyl-xanthyl and phenyl-pheno- β -naphtho-xanthyl. This, indeed, is very strange, the highly favorable influence of the xanthone ring is almost wholly offset by the naphthyl group in the ring, which group is otherwise even more favorable in its dissociation influence than the xanthone ring itself. More facts are needed before we can hope to unravel this confusing interplay of various influences.

The factors which influence the equilibrium between the monomolecular and the dimolecular phase of one and the same radical are, the nature of the solvent, the concentration of the solute, and the temperature of the solution. As regards the influence of the solvent, the evidence shows that it is in some instances appreciable. A comparison of the molecular state of substances at nearly the same concentrations in nitrobenzene, benzene and cyclohexane, all of which freeze at about the same

temperature, shows that, generally speaking, the dissociating influence of these solvents is in the order mentioned. Others also have found that, as compared with the other cryoscopic solvents, cyclohexane is very associating (4). More experimental work in this direction is desirable.

The remaining two factors, concentration of the solute and the temperature of the solution, have been investigated on so many examples that their influence is well established. This influence is in accord with what one would expect from the dissociation in general: the higher the concentration, the less is the molecular dissociation of the hexa-arylethane; also, the higher the temperature, the greater the dissociation of the ethane into monomolecular free radicals. Figure 2 brings out the influence of concentration of the solute on the degree of dissociation of several different triarylmethyls. Figures 3 and 4 bring out on two specific examples, each in a variety of solvents, the influence of the same factor, as well as the influence of temperature. The influence of each of these two factors is quite appreciable and is fairly uniform.

Molecular combinations. Triphenylmethyl combines with a variety of substances from most divergent classes of compounds. This property illustrates in a very striking manner the inherent unsaturated character of the free radical. These combinations are obtained merely by dissolving triphenylmethyl in the respective compounds, and when the solution has been cooled down to room temperature, the molecular combination, consisting of triphenylmethyl and solvent, crystallizes out. Molecular combinations of this nature were obtained with aliphatic and aromatic ethers, ketones, aldehydes, esters, nitriles; with ethylene oxide; with chloroform; with carbon disulphide, with aromatic hydrocarbons, with olefines, and even with saturated hydrocarbons such as heptane, decane, cyclohexane and methylcyclohexane. The combinations which are formed in this manner are readily dissociated into the component parts at a temperature near the boiling point of the volatile component. The fact that hexane and octane among the hydrocarbons tested, acetone among the ketones, methyl and ethyl formate among

the esters, fail to give additive compounds with triphenylmethyl, is to be interpreted in the sense that the dissociation temperature of these additive compounds is probably below ordinary room temperature.

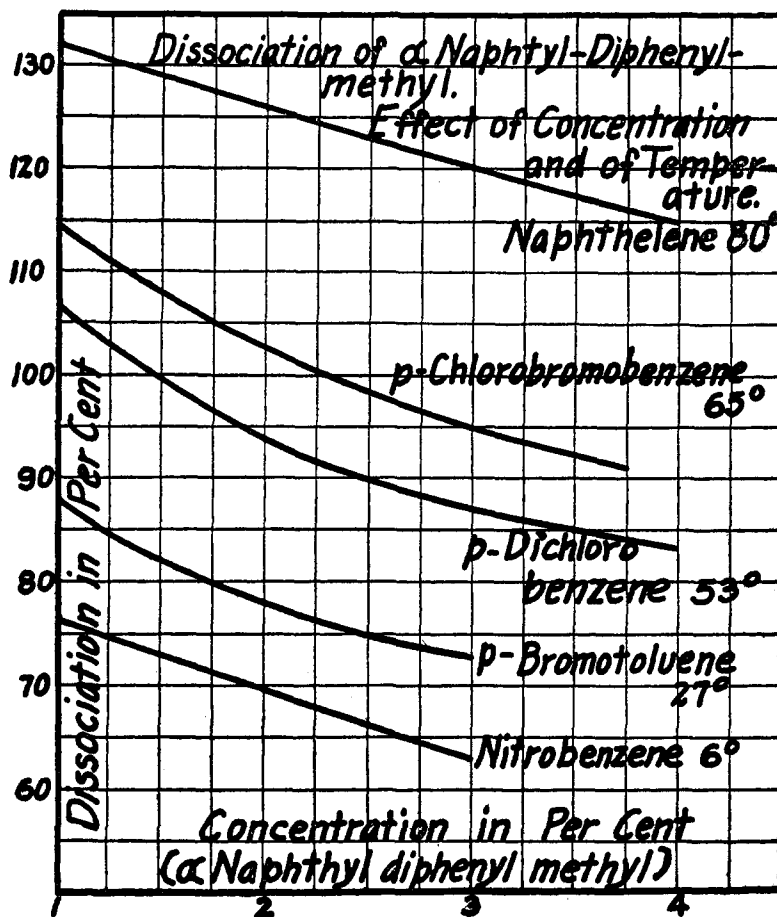


FIG. 3

The composition of the various additive compounds is always one mole of hexa-arylethane to one mole of the other component, except in case of decane where it appears to be $(R_3C) + C_{10}H_{22}$. It is this remarkable uniformity of composition of these combinations that raises doubt in one's mind whether they should

be considered merely as triphenylmethyl with solvent of crystallization. It would seem, were the latter the case, then the relative proportions of triphenylmethyl to the other component would vary with the nature of the latter. If not as solvent of crystallization, what function do these components play in the combinations? It seems rather difficult to find a plausible

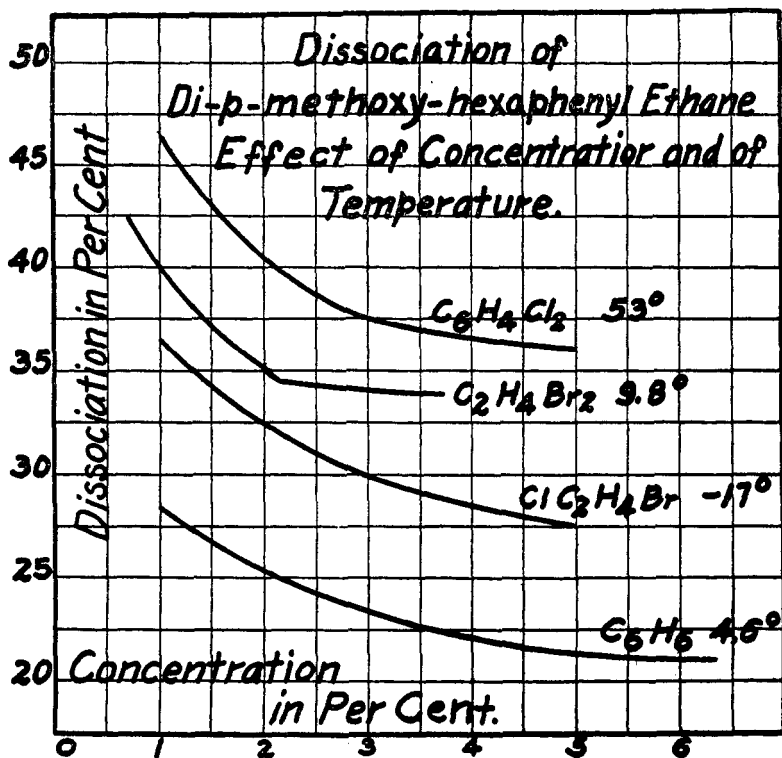
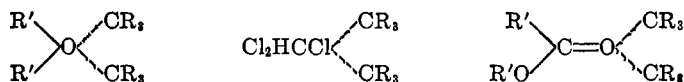


FIG. 4

explanation in terms of graphic formulas. In the esters, ketones, and aldehydes, we have the double linking $C = O$; in carbon disulfide, the corresponding $C = S$; while in the aromatic hydrocarbons and in the olefines, we have the grouping $C = C$. But it seems hardly probable that in all these instances triphenylmethyl adds itself in virtue of the double bond to the various compounds. If this were the case, we should expect the addi-

tion to result in fairly stable substances. But as a matter of fact, the addition compounds are extremely unstable, dissociating readily at temperatures of 50 to 100° into the original components. Indeed the stability of these additive compounds is apparently no greater than that of the additive combinations that result from triphenylmethyl with ethylene oxide, with ethers, with chloroform, all of which contain no double bond of any kind whatsoever.

An explanation in terms of the valence hypothesis for the existence of all the various additive compounds might still be had, if we are willing to assume that the oxygen, the sulfur, or the chlorine atom, as the case may be, functions as though it had acquired a higher valence than that which it ordinarily possess. Sulfur and chlorine are known to possess a variable valence, and of late it has become customary to consider that oxygen too, can acquire a higher than its usual valence state. We then have:



While such an explanation might perhaps account for the addition of the triphenylmethyl to ethers, esters, etc., the question still remains unanswered as to the mechanism of the addition of the free radical to completely saturated hydrocarbons, both aliphatic and alicyclic. And yet, these latter combinations are practically of the same order of stability as all the other combinations. Taking everything into consideration, we prefer, as Schmidlin does, to look upon all the additive compounds as "molecular combinations" wherein the second component is retained through the "residual affinity" in the triphenylmethyl molecule.

Another phase of this question deserves consideration. How shall we account for the fact that while triphenylmethyl forms such a wide variety of additive compounds, other triarylmethyls, which are monomolecular to a much greater degree than is triphenylmethyl, fail to give rise to such additive compounds?

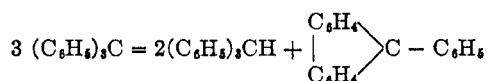
α -Naphthyldiphenylmethyl, β -naphthyldiphenylmethyl and *p*-methoxytriphenylmethyl are monomolecular to the extent of 70, 30 and 30 per cent respectively. They belong distinctly more to what we consider as the class of free radicals; consequently it would seem that they should produce molecular combinations more readily than triphenylmethyl does; and yet the reverse is the case. This apparent contradiction, however, is explainable to a large degree by the following considerations: At room temperature the dissociation of hexa-phenylethane is only about 5 per cent. In other words, the tendency on the part of triphenylmethyl to become saturated is evidenced through the temporary feeble attachment of one free radical to another, or through attachment to substances such as ethers, esters, ketones, hydrocarbons, etc., if these be present. On the addition to this system of slight amounts of energy from the outside as on gentle heating, the union is disrupted and the free radical is regenerated. Thus the obvious predilection of triphenylmethyl to assume the dimolecular state, and on the other hand 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 its carbon atom is of a low order of stability. And now consider from the same point of view diphenyl α -naphthylmethyl. It is monomolecular to the extent of 70 per cent even at 6°C., and the dissociation increases rapidly with the rise of temperature. Evidently, in this particular triarylmethyl the trivalence of carbon is of such a 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 the tendency to unite with other substances, such as esters, ethers, ketones, etc. Thus a high degree of dissociation of the hexa-arylethane is indicative of the fact that in the resulting triarylmethyl the affinity of the trivalent carbon atom is all utilized in internal combinations of the radical itself, and consequently there remains very little, if any, residual affinity for outside combinations of reversible nature, whether it be radical to radical or radical to something else. The explanation here given should be tested on various

hexa-arylethanes which cover a wide gradation of dissociation tendencies.

Chemical reactions

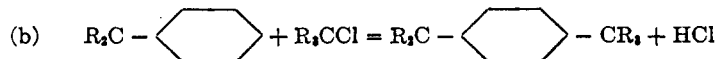
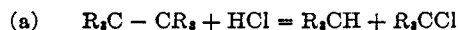
The triarylmethyls react readily with a great variety of substances, the reactions being as a rule irreversible. While many of the reactions have been studied in detail only on triphenylmethyl, still there is very little doubt that they are characteristic of the whole class of the triarylmethyls.

Effect of light. Even in the solid state, but especially so when in solution, the triarylmethyls are extremely susceptible to actinic rays. The darker the solution, the slower the decomposition, but it is advisable to avoid as much as possible exposure of any triarylmethyl to direct sunlight, or some decomposition may ensue. Like so many photochemical reactions, we have here also intermolecular oxidation and reduction:



The problem becomes more complex when the three aryl groups in the triarylmethyl are not all alike; the dehydrogenation and the consequent coupling of the two aryl groups may then occur in one or more of several possible ways. Only very few examples have been studied carefully in this connection.

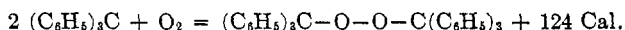
Effect of acids. It was thought at first that hydrogen chloride induces catalytically the conversion of triphenylmethyl into hexaphenylethane. Chichibabin, however, showed that the product is not hexaphenylethane but a stable isomer of it, namely benzhydryl-tetraphenylmethane. It is now, however, well established that the action of acids upon triarylmethyls is resolvable into two stages:



Whether the reaction will stop with stage (a) or proceed further with the formation of the benzhydryl according to (b), will

depend in each case upon the nature of the aryl groups. With triphenylmethyl, only 6 per cent of the total product is retained as given in equation (a) and the rest is converted into the benzhydryl; with diphenylmonobiphenylmethyl, according to Schlenk the reaction does not proceed further than the first stage; with diphenyl α -naphthylmethyl, as well as with *p*-methoxytriphenylmethyl, it is about 80 per cent according to (a) alone, and 20 per cent proceeds further according to (b).

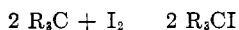
Formation of peroxides. The spontaneous oxidation of triarylmethyls with the formation of corresponding peroxides serves as an infallible test for the presence of a free radical. The absorption of oxygen takes place rapidly, as fast as by yellow phosphorus. The peroxides are colorless compounds, only slightly soluble in the usual organic solvents; they are fairly stable and possess characteristic decomposition points which are higher than the melting points of the corresponding free radicals or the carbinols. The precipitation of the peroxide when a solution of the free radical is exposed to air is of course accompanied by the decolorization of the solution. This oxidation is an exothermic reaction, and in the case of triphenylmethyl it is:



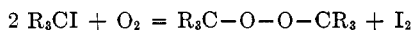
The amount of oxygen absorbed generally corresponds so nearly to the calculated that this reaction may serve as a basis for the quantitative estimation of the free radical. While the quantity of oxygen taken up by the radical is nearly the theoretical, the actual yield of the peroxide, however, varies with different triarylmethyls from 75 to 93 per cent, indicating that some decomposition of the peroxide must occur during its formation from the free radical. Indeed, even during the recrystallization of the peroxide from boiling benzene, slight decomposition is perceptible; in boiling xylene, at 140°, the decomposition of triphenylmethyl peroxide is complete.

Addition of iodine. The triarylmethyls unite with chlorine, bromine and iodine; while with the first two halogens both substitution and addition occurs, with iodine, addition alone

takes place. Next to peroxide formation, combination with iodine constitutes the most reliable identification reaction for the free radicals. The amount of iodine which is taken up is always short of the calculated, because these iodides are ever so much less stable than the corresponding bromides and chlorides, and there is a tendency on the part of the iodide to dissociate again into free radical and iodine:



This equilibrium varies with the individual members of the series, but it is usually reached when 60 to 80 per cent of the calculated amount of halogen has been taken up. The isolation of the iodides often presents difficulties, since they are readily decomposed by water, alcohol, and even by atmospheric oxygen:

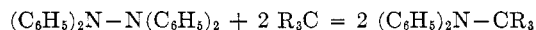


Irreversible addition reactions. There are many other reactions of triarylmethyls, which result in well defined derivatives of triarylmethane. Here again, most of the work has been done with triphenylmethyl, but the reactions are unquestionably typical of the whole class. They will be summarized briefly in Table 2:

TABLE 2

	PRODUCTS	OBSERVER
$R_3C + H$ (narcent)	R_3CH	Gomberg
$R_3C + H$ (in presence of Pt.)	R_3CH	Schmidlin
$R_3C + S$	Polysulfides	Schlenk
$R_3C + NO$	R_3CNO	Schlenk
$R_3C + NOCl$	$R_3CNO + R_3CCl$	Schlenk
$R_3C + NO_2$	R_3CNO_2	Schlenk
$R_3C + O:C_6H_4:O$	$R_3C-O.C_6H_4.O-CR_3$	Schmidlin
$R_3C + C_6H_5OH$	$R_3C-C_6H_5OH + R_3CH$	Schmidlin
$R_3C + C_6H_5(CH_3)_2$	$R_3C-C_6H_5(CH_3)_2 + R_3CH$	Wieland
$R_3C + NH_2NHC_6H_5$	$R_3C-C_6H_5NH.NHC_6H_5 + R_3CH$	Schlenk
$R_3C + CH_2N_2$	$R_3C-CH_2 - CR_3$	Schlenk
$R_3C + Na$	R_3CNa	Schlenk

It might be mentioned here that because of its preëminent tendency to make addition compounds, triphenylmethyl has found application as a reagent for the detection of free radicals other than triarylmethyls. For instance it reacts, as Wieland found, with tetraphenyl hydrazine, as follows:

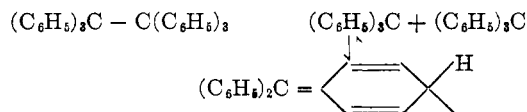


This reaction has been advanced as an argument in support of the hypothesis that tetraphenylhydrazine itself is in solution dissociated to some extent into two half-molecules, in other words into free radicals containing divalent nitrogen. A similar argument has been used in support of the assumption that dehydrophenols contain monovalent oxygen.

Relation between dissociation and color. Tautomerism of free radicals

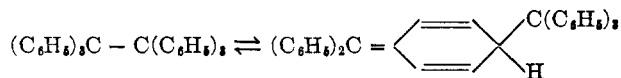
The fact that hexa-arylethanes, colorless in the solid state, give colored solutions in organic solvents has been explained, principally, along two different lines:

1. Colorless hexa-arylethanes, in solution, dissociate to form the colored free radicals. When the substance is colored also in the solid state it is then a free radical in that phase as well.
2. Dissociation occurs and is followed by tautomerization of the benzenoid triarylmethyl into the quinonoid monomolecular tautomer; the latter substance is the principal factor responsible for color production.



As has been previously mentioned in this paper, upon shaking a solution of triphenylmethyl with oxygen, the color vanishes, but reappears after a few seconds, and this phenomenon takes place several times before the solution is completely and permanently decolorized. By weighing the amount of peroxide formed in a single decolorization Schmidlin was able to calculate

the amount of the colored form which was present. His results indicated that the ratio of colorless to colored form was about 10 to 1. However, since the molecular weight of triphenylmethyl at room temperature corresponds very nearly to the dimolecular formula, Schmidlin concluded that the color must be due to the presence of some tautomeric form of hexaphenylethane and not to dissociation, as for instance:



Schmidlin also observed the variation in the intensity of color of triphenylmethyl solutions at different temperatures, and found that at the freezing point of chloroform, -63° , the color entirely disappeared. He conducted colorimetric determinations over a range of temperatures from the freezing point to the boiling point of benzene, and found that the color increased sixfold. From these results he concluded that the intensification of color of triphenylmethyl solutions with rise of temperature must be due to something other than dissociation. Wieland, Schlenk and Main took the very opposite point of view, assuming that hexaphenylethane is dissociated to some extent. Hence, according to them, the increase in color intensity is due entirely to dissociation of the ethane into free radicals.

What seemed to be the most convincing evidence in favor of the dissociation theory is found in the work of Piccard on the increase of color of triphenylmethyl solutions with dilution. This behavior constitutes a deviation from Beer's law, which states that the absorption of light by solutions should remain constant if there were no chemical changes on dilution. In the case of hexaphenylethane we are concerned with one of two phenomena: either tautomerism of the ethane without change of molecular weight, or dissociation, which leads to an increase of the number of molecules. If it were tautomerism the equilibrium would be between two isomers and, Piccard assumes, such an equilibrium would be independent of the dilution; but if it were dissociation, then the equilibrium would be between a polymer and the products of its dissociation—and such an equilibrium should be influenced by dilution. He conducted a series of experiments on hexaphenylethane

solutions and found a decided increase in color upon dilution. He therefore concluded that the phenomenon must be dissociation (5).

The occurrence of these three characteristic phenomena has been since verified on a large number of hexa-arylethanes. They were found to undergo, on oxidation, several successive decolorizations, to acquire intensification of color on dilution and to suffer a marked diminution in intensity of color when their solutions were cooled. In fact, the deviation by a substance from Beer's law has become an important, and often the only factor in the decision of designating the substance as a free radical.

We have, then, these two concomitant phenomena: on the one hand, the dissociation of hexa-arylethanes increases with their dilution and decreases with the lowering of the temperature of the solution; on the other hand, their color intensity also increases with their dilution and decreases with the lowering of the temperature of the solution. Hence the conclusion that dissociation and color production are related to each other as cause and effect.

Nobody can gainsay the general plausibility of this explanation. And yet, the question arises, is the change in color intensity which has been produced in the triarylmethyl strictly proportional to the increase in the monomolecular phase of the triarylmethyl? These two phenomena should, of course, be strictly parallel to each other if they be related as cause and effect. What little work of quantitative nature has been done on hexaphenylethane has led to contradictory conclusions, for the reason that this compound dissociates at room temperature but very little.

In di- β -naphthyl-tetraphenylethane the writer and Sullivan found a substance of very considerable and accurately measurable dissociation; its color, bright red in concentrated solutions shading to light yellow in dilute solutions, lends itself readily to colorimetric study; the substance is quite stable towards light; it is readily soluble in a variety of solvents throughout a wide range of temperature. In addition, it shows striking diminution of color within the temperature range of

ordinary cryoscopic determinations. On account of this fortuitous combination of properties, a study of this hexa-arylethane was made in an effort to throw more light on the relation which exists between color intensity and changes in the concentration or in temperature of the solutions of free radicals.

The molecular weight of the radical was determined in carbon tetrachloride ($-22^{\circ}\text{C}.$), ethylene chlorobromide (-17°), benzene ($+5.3$), nitrobenzene (5.7°), cyclohexane (5.8°) and *p*-bromotoluene (27°). Then, by the use of a properly constructed colorimeter, the effect of dilution on the color of the solution of the radical in benzene, nitrobenzene, and cyclohexane was determined; and secondly, the effect of temperature on the solutions of the radical in carbon tetrachloride and in toluene, covering a range, respectively of -22 to $+30$ and -40 to $+30$ was studied.

It was found that solutions of the free radicals in cyclohexane, benzene and nitrobenzene are of about the same intensity of color and the intensity of color changes equally in all cases on dilution, in spite of the differences in dissociation in these solvents. Assuming the color of a 5 per cent solution to be unity, we can calculate the relative intensity of color at dilutions down to 1 per cent in reference to this unit. Plotting these color values against the dilution, that is, the number of grams of the solvent containing 1 gram of the solute, we obtain curves a, b, c (fig. 5), showing the relative change of color intensity with dilution. Similarly, we assume the degree of dissociation at 5 per cent as our unit and calculate the relative degree of dissociation at other dilutions with reference to this unit. These values are also plotted against the dilution, and the resulting curves, a', b', c', show the relative change in dissociation on dilution. It is apparent, in nitrobenzene and benzene the intensity of color almost doubles with the decrease of concentration from 5 to 1 per cent, and yet the change in dissociation throughout the same range is very slight. On the other hand in cyclohexane, the dissociation increases three times as much as the color. This again shows that color is independent of dissociation, that is, an increase in dissociation may occur without an equal increase in color intensity.

It was found that a solution of the free radical in toluene at -40° or in carbon tetrachloride at its freezing point is only slightly colored although it is dissociated to the extent of from 15 to 20 per cent. On gradually warming these very light colored solutions an increase in color

begins to take place between -30° and -20° and this color increases 10 times with a rise of temperature of 50° while the dissociation increases only $\frac{1}{2}$ with the same change of temperature. If we assume as the unit

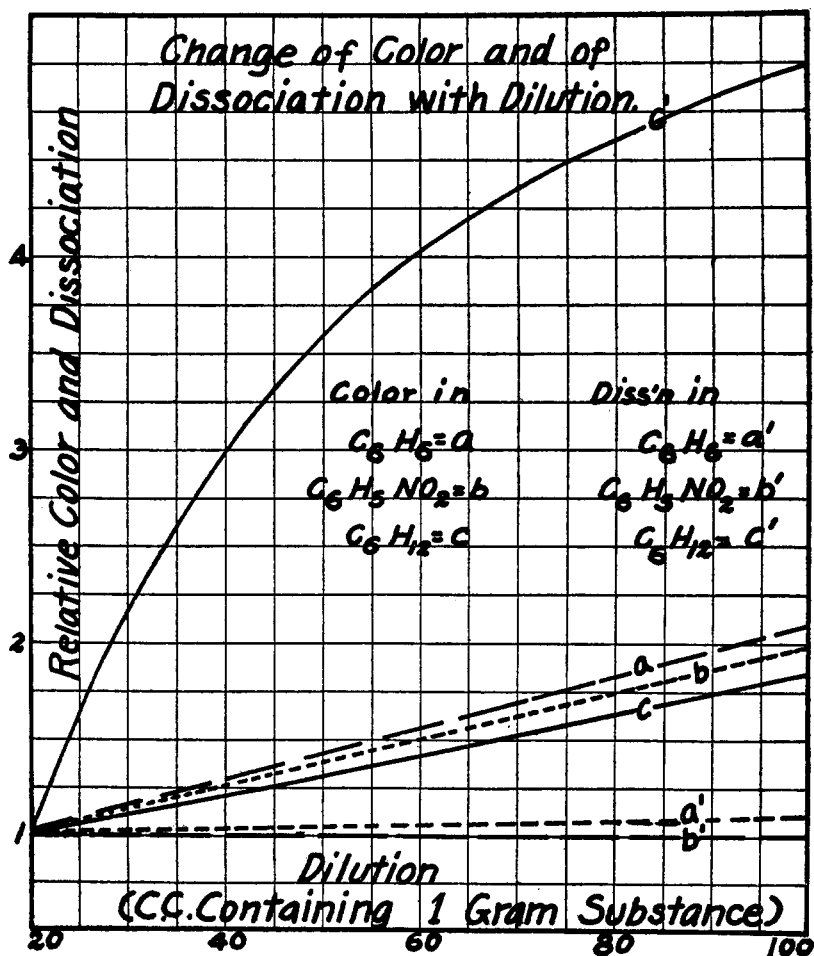


FIG. 5

of color intensity the color of a solution at -20° and calculate the relative color intensity at other temperatures with reference to this unit, then plot these values against temperature, we obtain curves a, b (fig. 6) showing the relative increase of color with temperature. If we now take as our unit of dissociation the amount of dissociation at -20°

we can calculate the relative dissociation at other temperatures with reference to this unit. Plotting these values against the temperature we obtain a curve *c*, showing the increase of dissociation with rise of temperature. The accompanying curves show the striking differences between the change in the degree of dissociation and the change in color

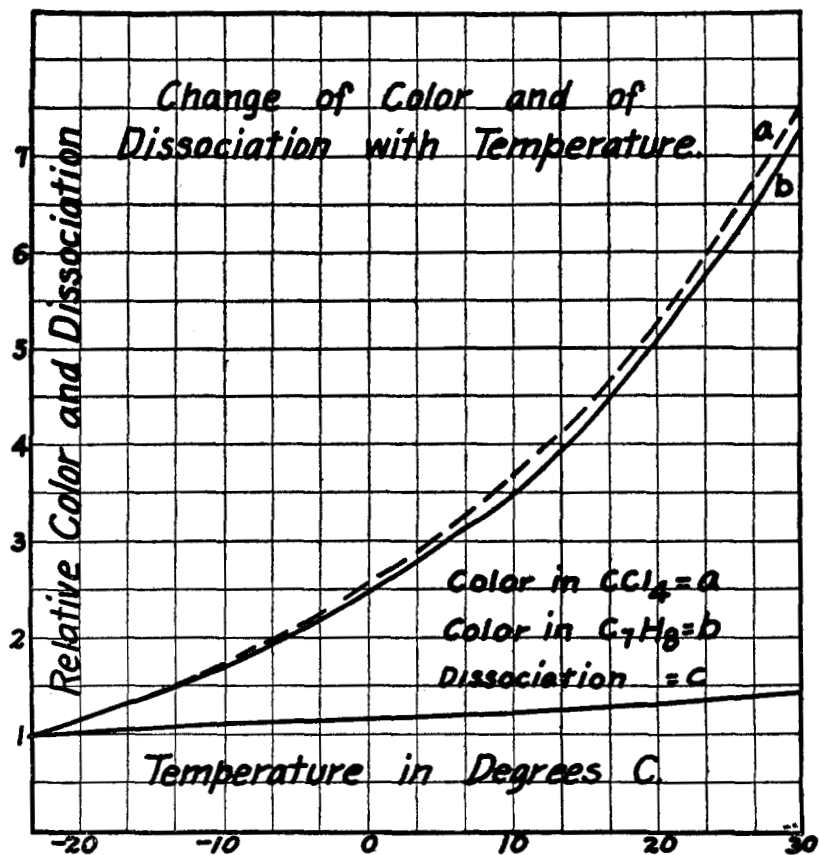


FIG. 6

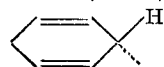
intensity which occurs when the temperature of the solution of the free radical is varied.

Three other triarylmethyls have been subjected to the same study by Mr. Forrester recently in this laboratory and the results obtained completely corroborate those with di- β -naphthyl-tetraphenylethane.

To sum up, the changes in color intensity of the hexa-arylethanes which result from variations in the concentration or in the temperature of their solutions proceed in the same direction as the changes of the dissociation do, but quantitatively they are not parallel to the changes in dissociation which are thus produced. These facts point to the conclusion that color of free radicals is not due wholly to dissociation of the hexa-arylethane into the tri-arylmethyl. The most satisfactory explanation of the facts is the hypothesis that following the dissociation we have tautomerization of the benzenoid triarylmethyl into the quinonoid form. The equilibrium between the hexa-arylethane and the triarylmethyl on the one hand and the equilibrium between the monomolecular tautomers on the other hand, are not equally influenced by changes either in concentration or in temperature. Not the trivalent state of the carbon atom, but rather the propensity towards quinoidation thereby brought about in the radical, is the cause of color-formation of the triarylmethyls.

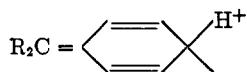
It must be admitted that colorimetric measurements give us only approximately quantitative results; and our findings should be verified by spectrometric measurements. Since, however, those who seek to connect directly color causation and dissociation in triarylmethyls depend merely upon qualitative colorimetric data, our quantitative measurements are certainly reliable to the extent of showing the inadequacy of that explanation. The pertinent statement of G. N. Lewis (6), that "the recognition of the existence of the quinonoid form is indispensable to an understanding of numerous reactions which characterize the hexa-arylethanes," should apply equally well to the free radical also—the recognition that the latter itself exists in a monomolecular quinonoid as well as benzenoid tautomer becomes indispensable.

The term triarylmethyl, then, may stand for any one of the three things: the ion $(R_3C)^+$, corresponding to the hydrogen cation, H^+ ; the benzenoid or quinoid radical R_3C or R_2C-



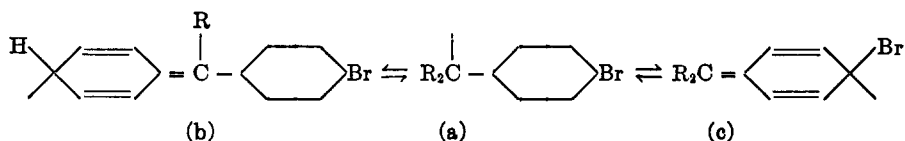
corresponding to atomic or nascent hydrogen, and

finally $(R_3C)_2$, corresponding to molecular hydrogen. It should be added that, according to H. I. Cole (7), the dissociation of hexaphenyl ethane from the viewpoint of the octet theory of valence, leads to the formation of the positive, colored ion



and the negative, colorless ion $[R_3C^-]$. From altogether different premises this interpretation has been arrived at by the writer some years prior.

Chemical evidence of quinoidation. Chemical evidence in favor of a tautomeric relation between a benzenoid and a quinonoid phase in the triarylmethyls has been gotten from the following considerations: Suppose we take a triarylmethyl in which at least one of the three aryl nuclei contains a bromine atom in the para position to the central carbon atom. The monomolecular phase of such a compound must exist, in conformity with what has been said above, in the following equilibrium state:



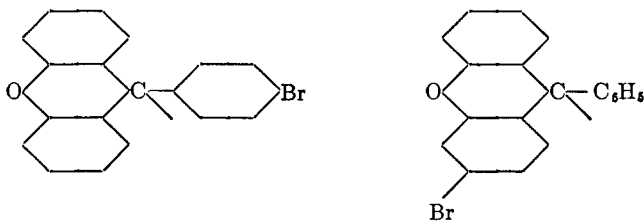
It is apparent that the bromine atom in the tautomer (c) plays a somewhat different function from that it possesses in the tautomers (a) and (b); in the latter two it is in a true benzene nucleus, and consequently it should not be readily detachable by metallic silver; but in the quinonoid tautomer (c), the bromine is linked to a carbon atom which resembles more aliphatic than aromatic state, and the halogen should therefore prove readily detachable from the carbon atom. Such is exactly the case. In compounds

of the type $\text{Br}-\text{C}_6\text{H}_4-\text{C} \begin{array}{l} \diagup \text{R}_2 \\ \diagdown \text{X} \end{array}$ ($\text{X} = \text{H}, \text{OC}_2\text{H}_5, \text{OH}, \text{etc.}$) which

are not subject to tautomerization, not a trace of bromine is taken out by treatment with metallic silver. And yet, when

the valence which holds X becomes free, as in the corresponding triarylmethyl, then the bromine is readily removable by silver. Surely such a remarkably striking change in function must have resulted only from a change in the constitution of the nucleus itself; a change to the quinonoid state appears to be the most rational explanation.

In conformity with the above explanation, it has proven possible in some instances to determine just which of the three aryl groups in the free radical assumes the quinonoid state. When the three aryl groups are independently linked to the central carbon atom, then each ring may assume a quinonoid phase, and the result is an equilibrium with three quinonoid tautomers, involving in each a different aryl nucleus. This has been shown to be the case with tri-p-brom-triphenylmethyl. But in those triarylmethyls which contain a xanthone ring, the latter is of paramount importance and is the dominating feature in the triarylmethyl. Consequently, when the process of tautomerism ensues, the quinoidation may not be directed equally towards all three nuclei. Of the two isomeric triarylmethyls,



only in the latter is the bromine atom removable by silver, as has been shown by experiment. Thus quinoidation must be occurring only in the two nuclei that constitute the xanthone ring. The same is true of thioxanthone derivatives. The work with acridines, which is being carried on by Mr. D. L. Tabern in this laboratory at the present time, has given results which confirm those previously obtained with xanthenols and thioxanthenols. Here quinoidation is localized preferentially in the acridine ring.

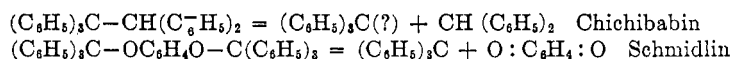
*Formation of triarylmethyls through dissociation of compounds
other than hexa-arylethanes*

The existence of triarylmethyls has been explained by the assumption that the three phenyl groups take up so much affinity from the central carbon atom that the remaining fourth valence functions with very little affinity. One is inclined to ask whether this is an explanation or merely a restatement of the facts in somewhat more strictly chemical nomenclature. Be that as it may, we know now of many cases where a triaryl-methyl group in combination with different groups becomes readily detached and assumes the existence of a free radical in exactly the same way as if it had come from a hexa-arylethane. In the following table, Table 3, are collected compounds which are known to undergo such dissociation. The experiments were largely limited only to triphenylmethyl compounds.

TABLE 3

SUBSTANCE—PRODUCTS OF DISSOCIATION	OBSERVER
$R_3CI \longrightarrow R_3C + I$ (at room temperature)	Gomberg (1900)
$R_3C-N=N-CR_3 \longrightarrow 2R_3C + N_2$ (at 0°)	Wieland
$R_3CNR_2 \longrightarrow R_3C + R_2N-NR_2$ (at 110°C)	Wieland
$R_3CCR_2CR_3 \longrightarrow R_3C + R_2C-CR_3$	Schlenk (1922)
$R_3C-S-CS-NC_6H_{10} \longrightarrow R_3C +$	Blicke (1923)
$R_3C-S-S-CR_3 \longrightarrow R_3C +$	Blicke (1923)

In the following instances, where the heating of the compound was done at temperatures at or above the decomposition temperature of triphenylmethyl, transitory color phenomena ensued suggestive of dissociation, but positive evidence is lacking that triphenylmethyl has actually been produced.

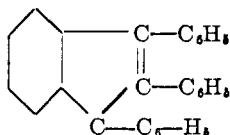


2. Trivalent carbon linked to less than three aryl groups

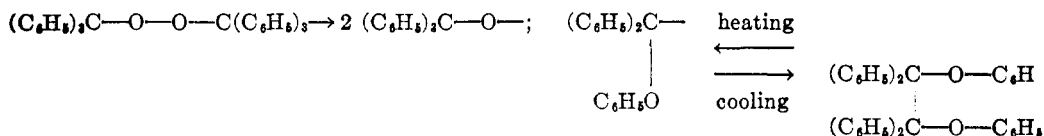
Many attempts have been made by different investigators to prepare compounds with trivalent carbon in the molecule, wherein the carbon atom is linked to less than three aryl groups.

With the exception of the metal-ketyls, which constitute a whole class of such substances, only isolated cases have been described. In no instance has the dissociation been as yet confirmed by the evidence of molecular weight determinations, and therefore the degree of dissociation is unknown.

Individual cases. Kohler, in 1908 found that 1, 2, 3-triphenylindyl bromide when treated with metals, gives a colored solution which becomes decolorized in air and a peroxide is formed. This constitutes a complete analogy in behavior with triarylmethyl halides. Consequently, a free radical must have resulted from the action of the metal upon the bromide. In that radical, the trivalent carbon atom is linked to two aryl groups, and the third valence, indicated in the formula by a heavy line, is linked not to an aryl group.



Wieland, in 1911, described the decomposition of triphenylmethyl peroxide in boiling xylene, at 138°. He formulates the reaction which occurs as follows:

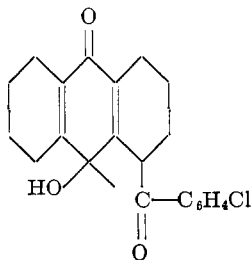


The intermediately produced radical with its monovalent oxygen is supposed to undergo instantly an internal rearrangement giving rise to diphenyl-phenoxyethyl, which, through union with a similar group, forms tetraphenyl diphenoxyethane; it is claimed that this latter compound resembles hexaphenylethane. It is colorless, dissolves colorless, but when its solution is heated to 80 to 100°, a color resembling that of triphenylmethyl is produced; on cooling, the solution becomes colorless. Peroxide formation by this new radical has not been observed; nor does the molecular weight indicate dissociation.

Gomberg and Jickling, in 1913, described diphenyl-thienyl-methyl chloride; this, when treated with molecular silver, gives rise to an intensely colored solution which absorbs oxygen from the air and in other ways shows the characteristic reactions observed on triarylmethyls. These findings have been corroborated recently by Mr. W. Minnis in our laboratory, but the free radical $(C_6H_5)_2C - C_4H_5S$, has proven so unstable that its isolation as such seems impossible. The close analogy of thiophene to benzene makes it appear probable that a radical of the above composition may exist.

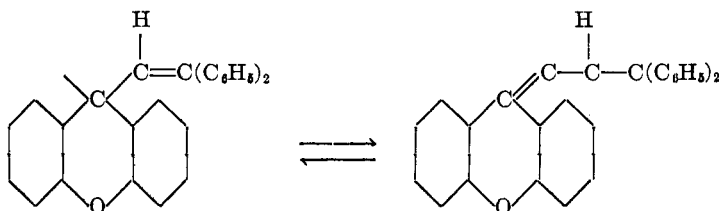
Cone, in 1912, has studied the N-alkyl iodide addition derivatives of quinoline and pyridine. He found these when treated with zinc, give colored solutions which absorb oxygen and behave in general as if they contain corresponding free radicals containing a trivalent carbon atom, or perhaps in equilibrium, radicals containing a tetravalent nitrogen atom. In view of the recent publication by Emmert and by Dimroth (8) it appears now probable that these substances are dipyridyl derivatives with no abnormal valence either on the carbon or nitrogen.

Scholl (9), in 1921, described what he considers to be the first example of a whole new peculiar class of compounds with trivalent carbon atom. The substance gives violet-blue solutions which become colorless on exposure to air. Protected from air, the substance is so stable that it will stand the temperature of boiling nitrobenzene, and it is monomolecular in that solvent under these conditions. Its constitution is, according to Scholl:

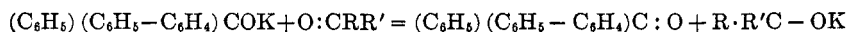


Ziegler and Ochs (10), in 1922, described an interesting example of what may prove to be a free radical wherein the trivalent

carbon atom is linked to two aryl groups and through the third valence to a secondary carbon atom.



Metal ketyls. R_2C-O-K . These constitute a large class of compounds which are formed through union of ketones with metallic sodium or potassium; they were first brought forward as a class of compounds containing a trivalent carbon atom by Schlenk in 1911. They are prepared, in some instances, through direct action of metallic sodium upon the diaryl ketone dissolved in ether, as has been done by Beckman and Paul as far back as 1894; but as Schlenk showed, a more general method consists in adding the previously prepared potassium compound of phenyl-biphenyl-ketone, which is quite soluble in ether, to an ethereal solution of any other ketone. As the majority of the metal ketyls are insoluble in ether, the following reaction ensues:

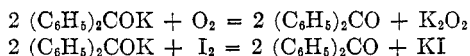


We thus have a class of compounds which are analogous to what Wieland considers his phenoxy-diphenylmethyl to be: $R_2C-O-C_6H_5$, with $-(OK)$ corresponding to (OC_6H_5) .

A large number of such metal ketyls have been prepared by Schlenk, not only from aryl ketones, but also from anthraquinone, xanthone, γ -benzopyrone, dimethyl pyrone, and a variety of other compounds containing the $C=O$ group.

It should be noticed, that a number of these metallic derivatives possess a composition which does not correspond to that anticipated from the structure of the ketones; not infrequently only half the calculated amount of metal is taken up by the ketone.

The metal ketyls are colored blue or green. They are readily affected by oxygen and by iodine, but the reactions are different from those shown by the tri-arylmethyl free radicals:



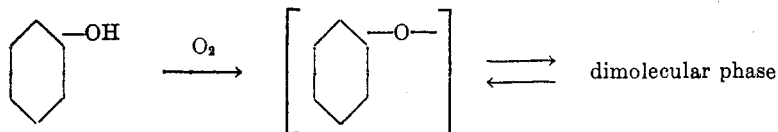
While the reactions indicate that we are dealing here with an extremely unstable class of metallo-organic compounds, the evidence is not as conclusive as might be desired that these are actually free radicals. Schmidlin looks upon them as loose "molecular" compounds between ketone and metal, which are formed in virtue of the residual affinity of the oxygen in the ketone, just as we have a large number of molecular compounds between ketones and metal halides.



Pentaphenylethyl. Schlenk (11) just recently described the exceedingly interesting radical, $\text{R}_3\text{C}-\text{CR}_2$. It constitutes an excellent example of a carbon atom in the trivalent state, two valencies being taken up by two aryl groups, but the third valence is in union with an aliphatic, tertiary carbon atom, i.e., the group $\text{R}_3\text{C}-$.

III. COMPOUNDS WHICH CONTAIN EITHER TRIVALENT CARBON OR MONOVALENT OXYGEN

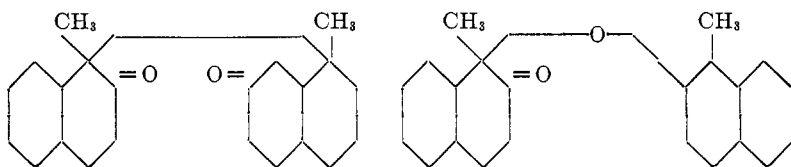
Dehydro phenols; ketomethyls or aroxyls. The first representatives of this class of unstable compounds were described by Pummerer and co-workers, then examples were discovered by Porter and Thurber (12), and very recently Stefan Goldschmidt (13) described still others. They are produced by mild oxidation of phenols, usually by means of potassium ferricyanide, and the reaction which is supposed to occur can be illustrated on the following hypothetical simple example:



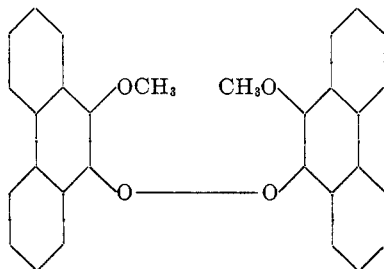
The products which result in this manner, in virtue of the dehydrogenation of the phenols, are known as "dehydrophenols." As a matter of fact, in practice it was found advisable, if not necessary, to use the more complex phenols, and particularly phenols that have one or both hydrogen atoms, ortho to the dyroxyl, replaced by some complex group. Pummerer used several naphthol derivatives, while Goldschmidt worked with phenanthraquinoles.

The questions under discussion concerning this class of substances are these: (1) What is the constitution of the dehydrophenols in their dimolecular phase? (2) To what extent, and under what conditions do the dimolecular dehydrophenols dissociate into monomolecular free radicals? (3) What is the constitution of the monomolecular compounds so produced—are they really radicals containing monovalent oxygen, or do they rearrange spontaneously into radicals with a trivalent carbon atom?

1. As regards the first query, agreement is lacking. Pummerer rejects the peroxide formula for the dimolecular dehydrophenols and prefers of the two remaining theoretically possible structures, the second to the first, i.e., the quinol ether structure (b) to the "ethane" structure (a).

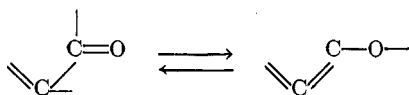


Goldschmidt, on the other hand prefers the peroxide structure, and formulates the dehydro-phenanthraquinol as (c)



2. Whichever be the true constitution of the dimolecular dehydrophenols, evidence is not wanting that, in solution, dissociation occurs. Unfortunately the deductions are based upon such low concentrations of the solute and consequently such small depression in the freezing point of the solvent, that the quantitative interpretation must be made with considerable reserve. Pummerer reports for his dehydrophenols, in concentrations of 0.25 per cent as high as 50 per cent dissociation. Goldschmidt finds that the dissociation of his phenanthroxyl compound is a time reaction, requiring about three hours before equilibrium is finally reached; at that stage the dimolecular modification of the methoxy and ethoxy ether derivative have dissociated to the extent of 40 per cent and 60 per cent respectively. In support of the contention that we are dealing here with the phenomenon of dissociation both Pummerer and Goldschmidt rely very much upon the fact that dehydrophenols, only slightly colored or entirely colorless in the solid phase, give like the hexa-arylethanes colored solutions, and that these solutions do not follow Beer's law: dilution of the solution leads to an intensification of color.

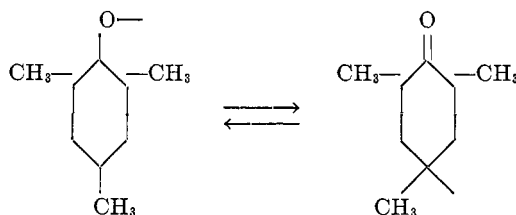
3. Outside of dissociation and of the color effects just mentioned, these radicals show very little resemblance to the triaryl-methyls. They are not readily affected by atmospheric oxygen; they do not unite with iodine; they however combine with triphenylmethyl. From a variety of considerations, the conclusion is drawn by Pummerer that these radicals exist in tautomeric equilibrium between the aroxyl and ketomethyl forms:



Goldschmidt, on the other hand, considers that the evidence is preponderatingly in favor of the radical with monovalent oxygen atom in the molecule.

Porter and Thurber described recently a most interesting instance of what seems to be a dehydrophenol of very simple composition. By oxidizing mesitol with silver oxide they

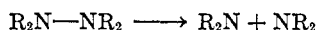
obtained a substance with an odd or unpaired electron, that is an unoccupied valence.



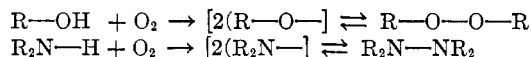
Further details will be expected with interest, especially in view of the opinion expressed by Goldschmidt to the effect that the oxidation product of mesitol is not a dehydrophenol.

IV. COMPOUNDS WHICH CONTAIN DIVALENT NITROGEN

Tetra-arylhydrazines. The fact that nitrogen exhibits in its inorganic compounds a variable valence from one to five, furnishes sufficient basis for the expectation that organic compounds also may be found in which nitrogen may be functioning as divalent rather than in its usual trivalent or pentavalent state. H. Wieland, from his extensive and excellent experimental work in the field of tetra-arylhydrazines, has concluded that we have in these compounds labile substances which are subject to dissociation similarly to hexa-arylethanes:



In these compounds we have remarkably close analogs to the above mentioned dehydro-phenols. Like the latter, so also are the tetra-arylhydrazines prepared by the action of mild oxidizing agents, and we might call them correspondingly "dehydroamines":

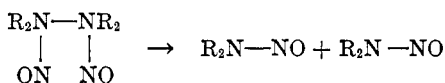


Of the some 15 tetra-arylhydrazines that have been described, only in one single instance was the dissociation sufficiently high at room temperature to be measured. The determination in

that case indicates a probable dissociation into the surmised

The two most typical reactions of hexa-arylethanes, namely the formation of peroxides, and the addition of iodine at room temperature, are not shared by the tetra-arylhydrazines.

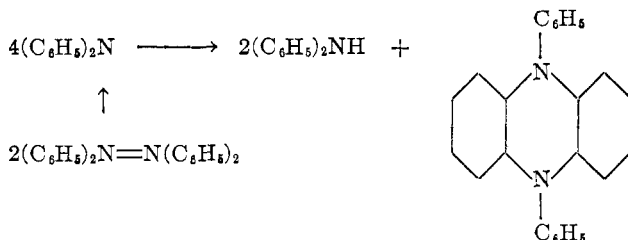
It is obvious that the three reactions of the aryl-hydrazines—spontaneous auto-oxidation and reduction, addition of nitric oxide and of triphenylmethyl, are nicely explainable on the assumption of previous dissociation into free diarylnitrogen radicals which possess at least a very brief period of temporary existence. But it must be conceded that this is not the only possible explanation of the mechanism of the above reactions. It is conceivable that auto-oxidation and reduction may occur within the whole tetra-arylhydrazine molecule and that it breaks subsequently to that into unequal parts; it is also conceivable that the addition of the unsaturated groups, NO or R_3C- , occurs, prior to the cleavage of the hydrazine molecule in virtue of the fact that the two nitrogen atoms in it, being trivalent have each still two potential valences at their disposal:



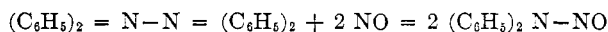
Thus, the chemical reactions which characterize the tetra-arylhydrazines, although they resemble those of the hexa-arylethanes, may be interpreted without necessarily assuming the independent existence of diaryl nitrogen radicals. The hydrazines themselves represent, to begin with, unsaturated systems, and therefore the case is somewhat different from that of the hexa-arylethanes. In the latter, we start with completely saturated molecules; hence the spontaneous union with iodine, oxygen, hydrogen, phenol, xylene, phenylhydrazine, etc., could not possibly occur unless the ethane does dissociate into radicals.

The physical behavior of tetra-arylhydrazines, however, presents more cogent evidence in favor of assuming dissociation into radicals. First, the tetra-arylhydrazines, although colorless, give rise to colored solutions, and the color is intensified when the solution is diluted or when its temperature is raised. This behavior is entirely analogous to that of the hexa-arylethanes.

The chemical reactions of the tetra-arylhydrazines are, in some respects, analogous to those of the hexa-arylethanes. When a solution is allowed to stand for some weeks, or when heated for a short time, decomposition ensues. The products which result suggest, first, that the hydrazine has split into two diarylnitrogen radicals; second, these interact, one radical becoming reduced at the expense of the other, just as under the influence of light, one triarylmethyl radical becomes reduced at the expense of the second; third, the dehydrogenated diaryl nitrogen radical polymerizes to a stable perazine product:



The second characteristic property of tetra-arylhydrazines is their reaction with nitric oxide, some combining with it at room temperature, others at elevated temperatures, forming fairly stable, but still dissociable, addition products:



Here again, one might infer that the addition of the nitric oxide occurs in consequence of a prior dissociation of the hydrazine into the active diphenyl nitrogen radicals, just as one assumes that the addition of nitric oxide to hexa-arylethane occurs because of the prior dissociation of the latter into triarylmethyl radicals.

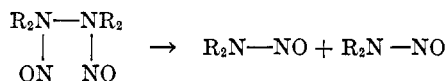
The third characteristic reaction is that tetra-arylhydrazines combine at room temperature, or at higher temperatures, with triphenylmethyl:



Here also, dissociation into diaryl-nitrogen may be assumed to have occurred previously to taking on the triarylmethyl.

The two most typical reactions of hexa-arylethanes, namely the formation of peroxides, and the addition of iodine at room temperature, are not shared by the tetra-arylhydrazines.

It is obvious that the three reactions of the aryl-hydrazines—spontaneous auto-oxidation and reduction, addition of nitric oxide and of triphenylmethyl, are nicely explainable on the assumption of previous dissociation into free diarylnitrogen radicals which possess at least a very brief period of temporary existence. But it must be conceded that this is not the only possible explanation of the mechanism of the above reactions. It is conceivable that auto-oxidation and reduction may occur within the whole tetra-arylhydrazine molecule and that it breaks subsequently to that into unequal parts; it is also conceivable that the addition of the unsaturated groups, NO or R_3C- , occurs, prior to the cleavage of the hydrazine molecule in virtue of the fact that the two nitrogen atoms in it, being trivalent have each still two potential valences at their disposal:

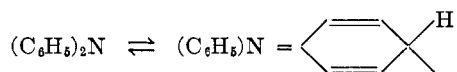


Thus, the chemical reactions which characterize the tetra-arylhydrazines, although they resemble those of the hexa-arylethanes, may be interpreted without necessarily assuming the independent existence of diaryl nitrogen radicals. The hydrazines themselves represent, to begin with, unsaturated systems, and therefore the case is somewhat different from that of the hexa-arylethanes. In the latter, we start with completely saturated molecules; hence the spontaneous union with iodine, oxygen, hydrogen, phenol, xylene, phenylhydrazine, etc., could not possibly occur unless the ethane does dissociate into radicals.

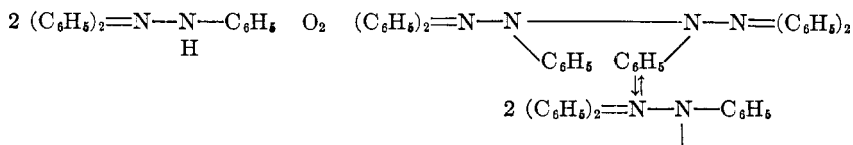
The physical behavior of tetra-arylhydrazines, however, presents more cogent evidence in favor of assuming dissociation into radicals. First, the tetra-arylhydrazines, although colorless, give rise to colored solutions, and the color is intensified when the solution is diluted or when its temperature is raised. This behavior is entirely analogous to that of the hexa-arylethanes.

If we exclude the possibility that the hydrazines tautomerize into some kind of quinonoid modification without change of molecular weight, then the color phenomena above cited are best ascribed to the fact that dissociation into radicals has occurred.

While there is at present no experimental evidence in favor of the assumption that the diaryl nitrogen radicals tautomerize into the quinonoid modification, the possibility of this occurring is not excluded. We would then have another instance of trivalent carbon, as in the dehydrophenols.



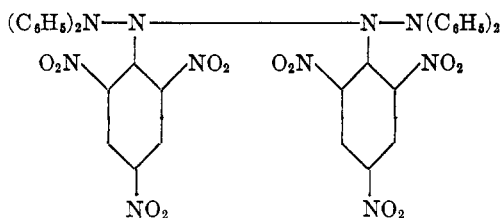
Triaryl hydrazyls. Quite similar to the tetra-arylhydrazines is the class of the remarkably unstable and very reactive substances known as the tetrazanes. They too, are made by dehydrogenation of complex amines by means of mild oxidizing agents such as lead peroxide, as for instance:



The tetrazanes so formed, according to Stefan Goldschmidt (14), are dissociable into two radicals; in the instance cited, one molecule of hexa-aryltetrazane dissociated into two triphenylhydrazyls.

In their chemical and physical behavior the tetrazanes resemble the tetra-arylhydrazines. They undergo when dissolved, spontaneous decomposition even at lower temperature than tetraphenylhydrazines. They unite with nitric oxide and with triphenylmethyl. Colorless in the solid stage, their solutions are green to blue, the color increasing in intensity when the solution is further diluted, or when its temperature is raised. Thus here again, the fact that the solutions of these substances do not follow Beer's law, seems to be the main argument in

support of the assumption that they are dissociable into radicals with divalent nitrogen. Molecular weight determinations in benzene have been made on four tetrazanes. Three are described as only slightly dissociable because they give only slightly colored solutions. While the results obtained from the molecular weight determinations would perhaps indicate some slight dissociation of these three tetrazanes, the author himself hesitates to draw this conclusion, because, as he says, decomposition of the compound might have ensued. The fourth tetrazane proved the most stable of all so far prepared:

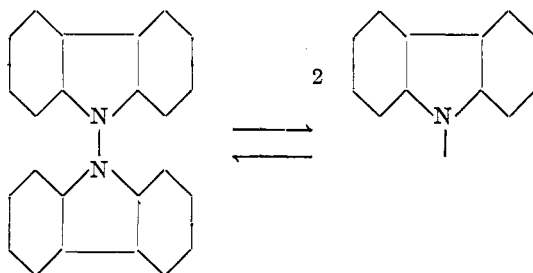


In the solid state it looks like potassium permanganate, its solutions are of violet color, not unlike that of the permanganate salt. From this as well as from the molecular weight of the substance (calculated 394; found, 335 on a concentration of 0.06 to 1.40 per cent, the conclusion is drawn that the tetrazane is dissociated in solution completely into the monomolecular radicals. And yet, what appears very strange, this particular tetrazane is the only one that does not respond to two of the most typical reactions for radicals with divalent nitrogen. It does not combine with nitric oxide at all, and the union with triphenylmethyl gives a combination not of the usual and the anticipated constitution.

From what has been said above, it is obvious that radicals with divalent nitrogen, such as diaryl nitrogen radicals and triaryl hydrazyls, probably do exist, but none the less more experimental evidence in favor of this view is much to be desired. Evidently we have here organic radicals which are far less stable than the triarylmethyls, and when they are produced at all, they have such a transitory existence that, from the experi-

mental side, the difficulties in handling and studying these elusive compounds becomes greatly enhanced.

A divalent nitrogen derivative of carbazole. Branch and Smith (15) have subjected carbazole to oxidation by means of silver oxide, and obtained a substance which closely resembles the diarylnitrogen radicals. It is colorless, gives rise to colored solutions, and has a molecular weight which indicates dissociation.

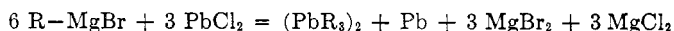


However, colorimetrically, it obeys Beer's law.

V. ABNORMAL VALENCE OF TIN AND LEAD

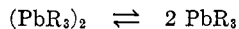
Mention must be made here of the interesting compounds of tin, described by Rugheimer in 1909. Hexa-ethyl tin gives a molecular weight in benzene which indicates partial dissociation into, presumably, radicals containing trivalent tin. With a concentration of 1.75 per cent of the compound, dissociation occurs to the extent of 50 per cent. The substance possesses a yellow color, and the solutions are slightly colored.

Krause and co-workers (16), in a series of papers, have quite recently described the preparation of several hexa-aryl plumbates: hexaphenyl, *o*- and *p*-hexatolyl, hexaxylyl, and hexacyclohexyl plumbate. Some are pale yellow, some pale green when solid, and they form colored solutions in organic solvents. They have been prepared under specific conditions in accordance with this reaction.



From the molecular weight determinations of these interesting compounds Krause concludes that while the hexaxylyl compound

does not dissociate appreciably, if at all, the other compounds mentioned do, especially in dilute solution:



Unfortunately, the total depression in the freezing point of the solvent occasioned in these experiments was of low order of magnitude, varying from 0.01 to 0.05°. The results suggest the occurrence of dissociation into radicals (PbR_3), but they can hardly be depended upon as furnishing a quantitative measure of the amount of dissociation.

As regards the chemical characteristics of these so called "triaryl lead" compounds, they absorb oxygen very slightly and give, with iodine, triaryl lead iodide.

VI. SULFUR AND ARSENIC WITH, POSSIBLY, ABNORMAL VALENCE

The many attempts of Lecher to prepare such diaryl sulfides that would dissociate, $\text{R-S-S-R} \rightleftharpoons 2 \text{R-S}$, and in this way give rise to radicals with monovalent sulfur, have not as yet proved successful. Although these disulfides actually give solutions which develop color on being heated, molecular weight determinations fail to indicate that dissociation into half molecules ensues.

Tetraphenyl-diarsine has been the subject of many investigations, in the expectation that this compound, in analogy with tetra-arylhydrazines, might perhaps dissociate into diaryl arsine, $(\text{C}_6\text{H}_5)_2 = \text{As}$. The results of the molecular weight determinations give no such indication, and the solution remains colorless even when heated. And yet, the substance absorbs oxygen, combines with iodine, manifesting an unsaturated character. P. Borgstrom and Margaret Dewar (17), however, draw the conclusion that "it may be said that the bond between the arsenic atoms of tetra-phenyl diarsine is easily broken. Divalent arsenic of the type $(\text{C}_6\text{H}_5)_2 = \text{As} -$ may be present in solution, but it is doubtful if it is the stable form. The valence or configuration of the stable form is unknown."

REFERENCES

The main results of the various investigations on organic radicals have become incorporated in the standard texts on organic chemistry. Consequently, it did not seem necessary to the writer of this paper to cite in detail the sources in the chemical journals. The following extensive reviews contain quite complete references to the publications up to 1914:

SCHMIDLIN, J.: "Triphenylmethyl," Ferdinand Enke, Stuttgart, 1913, XII + 233 pp.

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