5. *Free Radicals and Radical Stabililty. Part I. The Influence of the Phenoxyl Group on Radical Stability and Merisation.*

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For the purpose of ascertaining the influence of the phenoxyl group on the strength of the ethane linkage in tetraphenyldiphenoxyethane, the behaviour of the compound has been compared with that of hexaphenylethane and other dissociating systems. The stabilising influence of the phenoxyl group on the radical is considerably lower than that of a phenyl group, and the molecular weight of the substance in benzene is normal. In view of Schmidlin's criticism of Wieland's hypothesis that tetraphenyldiphenoxyethane dissociates into free radicals, the colour changes exhibited by the substance have been observed under a variety of conditions. These experiments show that dissociation occurs at high temperatures, but there is no exact reversibility in the colour changes owing to the formation of decomposition products.

Further evidence has been adduced to show the essential similarity in the dissociation phenomena of hexaphenylethane, diphenylbisdiphenylene-ethane, and tetraphenyldiphenoxyethane. The widely different reactivities towards oxygen are referred to the difference in merisation tendency which determines the rate of breaking down into free radicals. It is shown that the velocity of dissociation of diphenylbisdiphenylene-ethane is about twenty times greater than that of tetraphenyldiphenoxyethane. A general classification of free radical systems according to their merisation tendency is suggested.

Tetraphenyldiphenoxyethane does not absorb iodine at the ordinary temperature, but an absorption corresponding to 0·28 mol. occurs at 110°. The compound also reacts with sodium at the ordinary temperature to form the deeply coloured addition derivative analogous to sodium triphenylmethide, but the metal is without action on the isomeric triphenylmethyl peroxide under these conditions. Tetraphenyldiphenoxyethane is photochemically stable, and does not give coloured solutions in liquid sulphur dioxide. In this and other respects there is a marked similarity between this substance and diphenylbisdiphenylene-ethane.

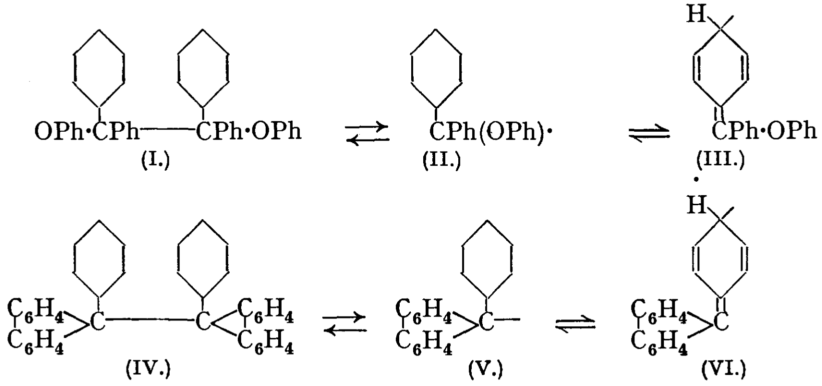
THE development of colour in hot solutions of tetraphenyldiphenoxyethane led Wieland (*Ber.*, 1911, **44**, 2550) to postulate a reversible thermal dissociation, analogous to that of hexaphenylethane apart from the fact that the amount of unimolecular radical is much lower :

$$\mathrm{OPh{\cdot}CPh_2{\cdot}CPh_2{\cdot}OPh} \rightleftarrows \mathrm{2CPh_2(OPh){\cdot}}$$

Schmidlin (" Das Triphenylmethyl," Stuttgart, 1914) criticised this view on the grounds that the evidence for the dissociation rests solely upon the generation of colour and that this alone is not sufficient to justify the assumption that free radicals are produced. In order to obtain further information on this point and, more particularly, to ascertain the influence of the phenoxyl group in these derivatives, the molecular state, colour, and reactivity of tetraphenyldiphenoxyethane have been examined under a variety of conditions.

Ebullioscopic determinations in benzene indicate that the dissociation of tetraphenyldiphenoxyethane is not of measurable magnitude at the b. p. of benzene. Wieland's observation that there are definite colour changes when the substance is heated in a high-boiling solvent in the absence of oxygen was confirmed. Although the intensity of the colour increases with temperature, there is no exact reversibility in the colour changes, and the postulation of a thermal dissociation does not therefore completely express the features observed. The colour depends, not only upon the temperature, but also upon the previous thermal treatment to which the solution has been subjected. Dissociation and decomposition phenomena are thus involved, and the substance is converted entirely into diphenyldiphenoxymethane and tetraphenylethylene at elevated temperatures.

A direct comparison of the thermal behaviour of tetraphenyldiphenoxyethane and diphenylbisdiphenylene-ethane reveals essentially similar features. Apart from the fact that the temperature at which colour is observed is lower by 25—35° and that there appears to be a truer approach to exact reversibility in the case of the latter, the behaviour of the two substances is analogous and is undoubtedly to be referred to the same cause. The dissociation of tetraphenyldiphenoxyethane (I) at 160° involves the production of the radical diphenylphenoxymethyl in much lower concentration than that of triphenylmethyl in the hexaphenylethane system at ordinary temperature. On the premises of the electronic theory of radical stability proposed by Burton and Ingold (*Proc. Leeds Phil. Soc.*, 1929, **1**, 421; *Trans. Faraday Soc.*, 1934, **30**, 52), it is clear that the contribution of the phenoxyl group to the stabilising effect is considerably lower than that of a phenyl group.



The colour of the solution may also be due to formation of the quinonoid modification (III). According to Gomberg and his school, the formation of quinonoid forms in the triarylmethyls increases with temperature much more rapidly than the degree of dissociation. These systems, however, have been examined at temperatures far removed from the temperature of incipient dissociation, *i.e.*, the temperature at which the ethane derivative begins to break down appreciably into free radicals. For example, it is known that a solution of triphenylmethyl in chloroform becomes colourless at —63°. A study of the available data leads us to believe that the quinonoid formation will largely vanish as the system approaches the temperature of incipient dissociation. It appears, therefore, that the behaviour of tetraphenyldiphenoxyethane at 160° is similar to that of hexaphenylethane at —63° and that formation of quinonoid structure occurs only at the higher temperatures preceding its decomposition into diphenyldiphenoxymethane and tetraphenylethylene.

The absorption of oxygen by the hexa-arylethanes is extremely rapid at room temperature and is usually accompanied by the discharge of the characteristic colour of the free radical and the formation of the corresponding triarylmethyl peroxide. We find that tetraphenyldiphenoxyethane also absorbs oxygen at ordinary temperature, but considerably more slowly than a typical radical system. Moreover, the solution, though initially colourless, becomes coloured at an early stage of the process and finally assumes a deep yellow colour when the oxidation is complete. The oxygen absorbed by hexaphenylethane corresponds quantitatively with the union of 1 mol. of the gas and the formation of a white peroxide and a yellow oil, each of composition $CPh_3{\cdot}O{\cdot}O{\cdot}CPh_3$. The oxidation of tetraphenyldiphenoxyethane, however, corresponds with the absorption of nearly 4 mols. of oxygen, and it is not possible to isolate the primary oxidation product. If, therefore, the initial oxidation is of the same character as that of hexaphenylethane, it is evident that the normal oxidation product $CPh_2(OPh)\cdot O\cdot O\cdot CPh_2\cdot OPh$ or its precursor $CPh_2(OPh)O\cdot O-$ is unstable and undergoes a further complex oxidation involving the absorption of nearly 3 mols. of oxygen. Triarylmethyl peroxides are generally stable towards oxygen at room temperature, but several cases are known where the free-radical system absorbs the gas in excess of the theoretical value. For instance, Gomberg and Forrester (*J. Amer. Chem. Soc.*, 1925, **47**, 2373) observed that the dimethoxytriphenylmethyls absorb more than 1·5 mols., and Conant and Evans (*ibid.*, 1929, **51**, 1925) reported an absorption of 2·5 mols. in the oxidation of certain substituted dixanthyls. These secondary reactions, however, take place comparatively slowly and may be disregarded in the discussion of the kinetics of the primary oxidation.

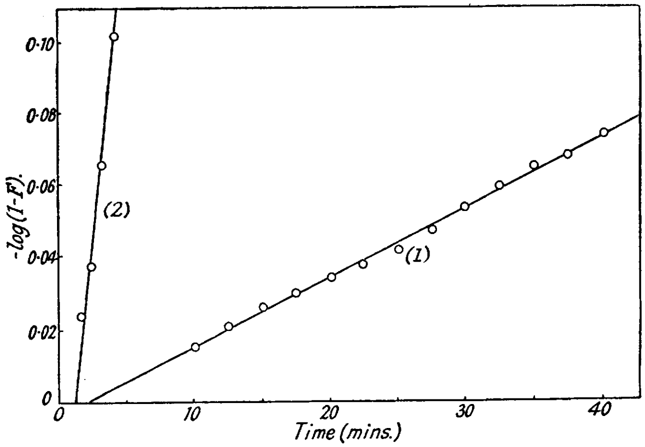
The amount of ethane derivative oxidised in unit time will depend chiefly upon (*a*) the rate of combination of oxygen with the unimolecular radical, (*b*) the amount of free radical in solution, and (*c*) the rate of dissociation of the ethane into free radicals. In the case of completely dissociated ethane derivatives, the rate of oxidation does not depend on (*c*), but in systems containing a low concentration of free radical this reaction may be the controlling one, as Conant and Evans (*loc. cit.*) have shown. Ziegler and his co-workers (*Annalen*, 1929, **473**, 163; 1930, **479**, 277; 1933, **504**, 182) have made precise measurements of the rate of dissociation by studying the reaction with iodine, nitric oxide, and oxygen. The kinetics of reaction with oxygen reveal that the process is complex, since the gas reacts, not only with the free radical, but also to some extent with the ethane. The interaction of triphenylmethyl and iodine furnishes an exact method of measuring the speed of dissociation, but unfortunately the method cannot be applied to tetraphenyldiphenoxyethane, since it does not react with the halogen at room temperature. According to Mithoff and Branch (*J. Amer. Chem. Soc.*, 1930, **52**, 255), the rate of oxidation of triphenylmethyl in carbon tetrachloride solution is proportional to the concentration of the hexaphenylethane and to a complicated function of the oxygen pressure, whereas Conant and Evans found that the rate of oxidation of the dixanthyls is independent of the latter factor. The behaviour of tetraphenyldiphenoxyethane in this connexion, and the question of the activation energy of the reaction, will be discussed in a further communication.

Apart from these considerations, however, we may employ the term " merisation tendency " to designate the fundamental characteristic of an ethane derivative of dissociating into radicals. The term is thus to be connected with the rate of dissociation of the ethane derivative in a system in which the concentration of the free radical is maintained at zero. This concept leads to the arbitrary division of free-radical systems into two general classes : (i) systems in which the merisation tendency is high, as in the case of hexaphenylethane; (ii) systems in which the merisation tendency is low, as in tetraphenyldiphenoxyethane. On this basis the difference in the speed of reaction with oxygen, etc., is to be referred to the difference in merisation tendency, since this determines the rate of equilibration of the system. In one experiment at 18° a solution of hexaphenylethane absorbed 1 mol. of oxygen in 3 mins., whereas the corresponding absorption in the case of tetraphenyldiphenoxyethane required 3 hours.

The merisation tendency of diphenylbisdiphenylene-ethane (IV) is considerably lower than that of hexaphenylethane, and a comparison was therefore instituted between the former and tetraphenyldiphenoxyethane. The fraction (F) of the ethane oxidised is a measure of the rate of dissociation, and by plotting the expression $-\log(1-F)$ against the time, as in Fig. 1, it is possible to obtain the value of k, the velocity constant of the dissociation. The value for diphenylbisdiphenylene-ethane is affected by the circumstance that accurate measurements of the rate of oxygen absorption could not be made owing to the rapidity with which the reaction takes place. However, the estimate based on the slope of the curves shows that the rate of dissociation is nearly 20 times greater than that of tetraphenyldiphenoxyethane.

The Prussian-blue test developed by Conant and Evans (*loc. cit.*) furnishes a further indication of the great difference in the rates of oxidation of diphenylbisdiphenylene-ethane and tetraphenyldiphenoxyethane. Reduction of ferric chloride is effected by the former substance in 1—2 mins. and by the latter in 10—15 mins. If we assume that the reaction proceeds through the free-radical mechanism, these values are likewise determined by the merisation tendency of the ethane derivative. The dissociation phenomena in the case of these two substances may therefore be summarised as follows :

FIG. 1.



(1) *Tetraphenyldiphenoxyethane.*
(2) *Diphenylbisdiphenylene-ethane.*

	Velocity constant of dissociation, $k \times 10^3$.	Time for Prussian-blue test, mins.	Temp. for generation of colour.
Diphenylbisdiphenylene-ethane ...	85·4	1—2	*ca.* 130°
Tetraphenyldiphenoxyethane	4·4	10—15	*ca.* 160

Although hexaphenylethane reacts rapidly with iodine to form an equilibrium mixture containing about 80% of triphenylmethyl iodide, the absorption of iodine by benzene solutions of tetraphenyldiphenoxyethane is negligible during 24 hours at room temperature. However, as observed by Professor Blicke (private communication), hot xylene solutions of the compound absorb iodine very rapidly. According to the present measurements, the absorption of iodine at 110° amounts to 28% of the theoretical value corresponding with the formation of diphenylphenoxymethyl iodide. In this connexion, it is significant that iodine is not absorbed by diphenyldiphenoxymethane under similar conditions.

The treatment of an ethereal solution of hexaphenylethane with sodium leads to isomerisation and the production of *p*-benzhydryltetraphenylmethane (Schlenk and Marcus, *Ber.*, 1914, **47**, 1678), and it is necessary to treat triphenylmethyl chloride with sodium amalgam in order to prepare sodium triphenylmethide. When a suspension of tetraphenyldiphenoxyethane in ether is shaken with sodium powder in an inert atmosphere, the colourless solution becomes yellow, and is deep red after a few days owing to the formation of the highly reactive sodium derivative. The isomeric triphenylmethyl peroxide, however, does not react appreciably with sodium under these conditions.

The fact that solutions of hexa-arylethanes in ionising solvents such as liquid sulphur dioxide are intensely coloured and contain the corresponding triarylmethyl ions led us to examine the behaviour of tetraphenyldiphenoxyethane and diphenylbisdiphenylene-ethane in this solvent. The solubility of both substances is, however, very low, and the solutions are colourless and non-conducting. Finally, in view of the comparatively rapid photochemical autoxidation and reduction of hexaphenylethane in non-ionising solvents, the possibility of a similar reaction in the case of tetraphenyldiphenoxyethane was also examined, but no appreciable photodecomposition was observed on exposure of the solutions to sunlight.

EXPERIMENTAL.

Tetraphenyldiphenoxyethane.—A benzene solution of pure triphenylmethyl chloride was reduced to the free radical by shaking it with excess of mercury in a sealed vessel for several hours (Gomberg, *J. Amer. Chem. Soc.*, 1900, **22**, 757). After standing overnight, the yellow solution was siphoned through a filter, and air passed through the filtrate to oxidise the free radical. The precipitated triphenylmethyl peroxide, m. p. 179°, was slightly yellow, but after being washed with warm acetone it was sufficiently pure for the next operation.

The conversion of the peroxide into tetraphenyldiphenoxyethane was carried out by heating the finely-powdered material (10 g.) with xylene (30 c.c.) for 8 mins. in an atmosphere of carbon dioxide and then adding absolute alcohol (35 c.c.), as recommended by Wieland (*loc. cit.*). All the operations were conducted in an atmosphere of carbon dioxide purified as described by Bowden and Jones (J., 1928, 1154). Recrystallised from benzene, the tetraphenyldiphenoxyethane formed perfectly white crystals, m. p. (vac.) 214·5—216°.

Diphenylbisdiphenylene-ethane.—A solution of pure triphenylmethyl chloride (15 g.) in dry benzene (100 c.c.) was shaken with pure mercury (8 c.c.) in a sealed bottle. After standing for several hours to allow mercurous chloride to settle, the solution was slowly siphoned under carbon dioxide into a flask, which was then hermetically sealed. The yellow solution of triphenylmethyl was exposed to bright sunlight for 2 or 3 days until it was almost completely decolorised (Schmidlin and Garcia-Banus, *Ber.*, 1912, **45**, 1344; Bowden and Jones, *loc. cit.*). The white crystals of diphenylbisdiphenylene-ethane which separated during the latter stages of the photodecomposition were recrystallised from benzene in an atmosphere of carbon dioxide and melted at 225°.

Molecular Weight of Tetraphenyldiphenoxyethane in Benzene.—These ebullioscopic determinations were carried out by the method of electrical heating while a slow stream of oxygen-free nitrogen was passed through the apparatus. The substance dissolved rapidly in the boiling solvent, and readings of the b. p. were taken as soon as dissolution was complete. With a solute concentration of 3·7%, the values of M obtained in the course of 3 mins. were 533, 521, 494; mean, 516 (Calc.: M, 518). This method thus affords no indication of the dissociation of the substance under these conditions.

Colorimetric Experiments.—(a) *Xylene solutions.* Tetraphenyldiphenoxyethane dissolved slowly in xylene at 80°, and in the absence of oxygen the solution remained colourless for about an hour at 100°, but finally assumed a pale brownish-yellow colour, which was not discharged on cooling to the ordinary temperature. When tetraphenyldiphenoxyethane was dropped into boiling xylene (138°) the solution was lemon-yellow with a pronounced pinkish tinge. On rapid cooling, the intensity of the colour decreased, but the solution did not become colourless even at 0°.

(b) *Naphthalene solutions.* The substance dissolved readily in naphthalene at 80° to yield a colourless solution. When the temperature was raised to 100°, the 2% solution became pale brown after 40 mins. When the solidified solution was kept at room temperature for 2 hours and again remelted, the first runnings of the melt were pale yellow.

Two experimental tubes were charged with equal amounts of naphthalene, and the temperature raised to 100° before addition of equal quantities of tetraphenyldiphenoxyethane under nitrogen. After the tubes had been heated in separate baths to 150°, one tube was maintained at this temperature while the other was cooled to the freezing point of the solution. There was a pronounced loss of colour in the latter, but the solution assumed its former colour intensity when re-heated to 150°. Rigorous colorimetric tests for reversible dissociation cannot be applied, but the intensification of the colour at the higher temperatures is undoubtedly due to the fission of tetraphenyldiphenoxyethane into free radicals.

(c) *Ethyl benzoate solutions.* With a similar procedure, finely powdered tetraphenyldiphenoxyethane was added to pure ethyl benzoate at 100° in an atmosphere of carbon dioxide, and the temperature raised rapidly (5 mins.) to 200°. The solution became pale brown at 150°; the colour deepened at 160°, became very intense at 175—180°, and acquired a definite reddish tinge near 200°. Rapid cooling of the solution from this point led to a marked decrease in the colour intensity, but the solution was still coloured on reaching room temperature.

Similar experiments carried out with diphenylbisdiphenylene-ethane under carbon dioxide showed a like behaviour. The solution was yellowish-brown at 115°, and the colour intensity at 135° was comparable with that of tetraphenyldiphenoxyethane at 160°. The intense golden-brown colour at 150° became deeper as the temperature was raised to 200°. On rapid cooling, the above changes were in a large measure reversed, and a practically colourless solution was finally realised at the ordinary temperature.

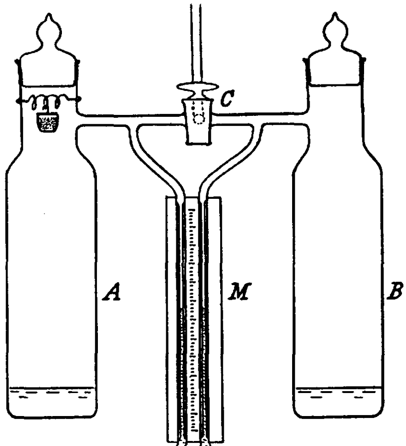
Oxidation of Tetraphenyldiphenoxyethane.—Wieland observed (*loc. cit.*) that solutions of tetraphenyldiphenoxyethane become yellow on standing in the air. Our preliminary experiments were therefore undertaken for the purpose of ascertaining the amount of oxygen absorbed per mol. of tetraphenyldiphenoxyethane and comparing the rate of oxidation with that of a typical hexa-arylethane.

The measurement of the oxygen absorption was carried out in a modification of Gomberg and Schoepfle's apparatus (*J. Amer. Chem. Soc.*, 1917, **39**, 1661), and the solution was mechanically shaken in contact with pure oxygen. The solvent employed was freshly-distilled bromobenzene, which also served as manometric liquid. The apparatus was placed in a chamber, thermostatically controlled at 18°, and the volume of oxygen absorbed measured at suitable intervals. Correction was applied for the vapour pressure of bromobenzene, and the results of a representative experiment are given below, the volume of oxygen absorbed having been reduced to N.T.P. (Formation of the true peroxide requires an absorption of 9·2 c.c.)

Time, hrs.	3	9	19	22	28	32	43	76
O_2 absorbed, c.c.	9·3	11·1	16·2	17·9	19·2	22·2	24·1	27·9
Time, hrs.	80	91	94	97	100	116	134	144
O_2 absorbed, c.c.	28·6	28·7	28·8	29·0	29·1	30·5	32·6	34·4

The oxidation process is complex but there are two fairly well-defined stages. During the comparatively rapid primary oxidation process the solution becomes yellow, but no insoluble peroxide is formed as in the case of triphenylmethyl. Attempts were made to isolate the primary oxidation product by allowing tetraphenyldiphenoxyethane to react with the theoretical amount of oxygen corresponding to the absorption of 1 mol. The solution was then transferred to a vacuum desiccator charged with freshly activated silica gel. The dark, oily residue thus obtained could not be induced to crystallise, and gave no solid product on trituration with the usual solvents. It is evident, therefore, that the stability of diphenylphenoxymethyl peroxide is much lower than that of triphenylmethyl peroxide. For comparison purposes the rate of oxidation of hexaphenylethane was determined in the same apparatus under similar conditions, and it was found that an absorption corresponding to 0·985 mol. occurred within 5 mins.

FIG. 2.



The properties of diphenylbisdiphenylene-ethane appear to indicate that its merisation tendency is lower than that of hexaphenylethane, and for this reason it was chosen for further comparison with tetraphenyldiphenoxyethane. The reactivities of these radical systems were compared by measuring the rates of oxygen absorption in the apparatus shown in Fig. 2. The two cylinders *A* and *B* (with thick, flattened ends) are closed with carefully ground glass stoppers, and are connected *via* the three-way stopcock *C* with a short capillary manometer *M*, which is fitted with a small steel scale for reading the pressure difference. The apparatus is fixed to a rack which can be immersed in a thermostat at 25° ± 0·02° and oscillated at high speed by means of a motor.

The manometer was partly filled with bromobenzene, and the same liquid (3·5 c.c.) was introduced into each cylinder. After the liquid had been saturated with oxygen, the finely powdered tetraphenyldiphenoxyethane (0·15 g.) was placed in a small glass basket (provided with a light cover-slip) and suspended from a wire fixed below one of the stoppers. After the stoppers had been sealed in position by means of sealing wax, the apparatus was shaken in the thermostat for 30—40 mins. to establish equilibrium in the two limbs. The rack was then lifted momentarily from its point of suspension and given a sharp jerk, so that the basket containing the ethane was precipitated into the liquid. At this instant a stop-watch was started, and the pressure difference registered by the manometer was read at intervals. The same rate of agitation was maintained throughout the experiment. Tetraphenyldiphenoxyethane takes an appreciable time to dissolve in bromobenzene at 25° and the early readings are slightly low on this account. The fraction *F* of the ethane oxidised under these conditions is given by the relation

$$F = \frac{v(0{\cdot}0054B - 0{\cdot}0054P + v) - (0{\cdot}0027)^2(p/9{\cdot}05)^3}{(v + 0{\cdot}0027p/9{\cdot}05)\boldsymbol{R}T} \cdot \frac{M}{w}$$

where v is the total of oxygen above the liquid in each limb of the apparatus, B the barometric pressure, P the vapour pressure of bromobenzene, p the pressure difference in mm. of bromobenzene, $\boldsymbol{R}$ the gas constant, T the absolute temperature, M the molecular weight of the ethane, and w the weight employed in the experiment. The terms containing $0{\cdot}0027p/9{\cdot}05$ may be neglected for the range of the present experiments. The results of typical experiments with tetraphenyldiphenoxyethane and diphenylbisdiphenylene-ethane are given below, t being the time (in mins.) :

<table>
<tr><th><i>t.</i></th><th><i>p.</i></th><th><i>F.</i></th><th><i>t.</i></th><th><i>p.</i></th><th><i>F.</i></th><th><i>t.</i></th><th><i>p.</i></th><th><i>F.</i></th><th><i>t.</i></th><th><i>p.</i></th><th><i>F.</i></th></tr>
<tr><td colspan="12">Weight of tetraphenyldiphenoxyethane = 0·015 g.
$F = 0{\cdot}005766p$; $k = 4{\cdot}4 \times 10^{-3}$.</td></tr>
<tr><td>5·0</td><td>4·0</td><td>0·023</td><td>15·0</td><td>10·0</td><td>0·058</td><td>27·5</td><td>18·0</td><td>0·103</td><td>37·5</td><td>25·0</td><td>0·144</td></tr>
<tr><td>7·5</td><td>5·0</td><td>0·029</td><td>17·5</td><td>11·5</td><td>0·066</td><td>30·0</td><td>20·0</td><td>0·115</td><td>40·0</td><td>27·0</td><td>0·156</td></tr>
<tr><td>10·0</td><td>6·0</td><td>0·035</td><td>20·0</td><td>13·0</td><td>0·075</td><td>32·5</td><td>22·0</td><td>0·127</td><td>42·5</td><td>29·0</td><td>0·167</td></tr>
<tr><td>12·5</td><td>8·0</td><td>0·046</td><td>22·5</td><td>14·4</td><td>0·083</td><td>35·0</td><td>24·0</td><td>0·138</td><td>45·0</td><td>31·0</td><td>0·178</td></tr>
<tr><td colspan="12">Weight of diphenylbisdiphenylene-ethane = 0·015 g.
$F = 0{\cdot}004819p$; $k = 85{\cdot}45 \times 10^{-3}$.</td></tr>
<tr><td>1·0</td><td>3</td><td>0·015</td><td>2·0</td><td>11</td><td>0·053</td><td>2·5</td><td>17</td><td>0·082</td><td>4·0</td><td>43</td><td>0·210</td></tr>
<tr><td>1·5</td><td>7</td><td>0·034</td><td></td><td></td><td></td><td>3·0</td><td>29</td><td>0·140</td><td></td><td></td><td></td></tr>
</table>

The results are not so reliable for diphenylbisdiphenylene-ethane owing to the comparatively rapid oxidation.

A further indication of the difference between the two ethane derivatives was furnished by the Prussian-blue test (Conant and Evans, *loc. cit.*). A solution of the substance in chloroform or carbon tetrachloride was vigorously shaken with a dilute solution of ferric chloride and potassium ferricyanide for 1 minute, and the time required for the appearance of a blue ring at the liquid–liquid interface observed. A positive test was obtained with diphenylbisdiphenylene-ethane after 1—2 mins., but tetraphenyldiphenoxyethane required about 10—15 mins. If the reaction involves the oxidation of the free radical, these figures are proportional to the rates of dissociation of the two ethane derivatives.

Absorption of Iodine.—It has been shown by Gomberg (*J. Amer. Chem. Soc.*, 1901, **23**, 486) that solutions of hexa-arylethanes absorb iodine at ordinary temperature. Under similar conditions we found no absorption of iodine when a solution of tetraphenyldiphenoxyethane in benzene was treated with 0·05N-iodine solution in a nitrogen-filled apparatus provided with a stirrer. The addition of one or two drops of the standard iodine solution gave rise to a blue coloration, which was not discharged on stirring or even on standing for 24 hours in an inert atmosphere. Similar experiments carried out with hexaphenylethane solution of the same concentration showed that the absorption of iodine is extremely rapid in the initial stages.

The following experiments were carried out with xylene solutions of tetraphenyldiphenoxyethane in an apparatus provided with a reflux condenser, a small burette containing standard iodine solution, and an inlet tube for the admission of air-free carbon dioxide. By means of a control experiment it was possible to follow very slight changes in the colour of the solution after the addition of iodine. Tetraphenyldiphenoxyethane (0·2 g.) was dissolved in 25 c.c. of xylene (purified by boiling over sodium), and the colourless solution maintained at 110° in a bath of pure sulphuric acid. The addition of iodine was followed at first by the rapid disappearance of the characteristic blue colour. The solution assumed a yellow colour on further addition of iodine and became reddish-brown after the introduction of 3·5 c.c. and garnet-coloured after 4·5 c.c. In view of the fact that in the control experiment the addition of 0·3 c.c. of the iodine solution to 25 c.c. of xylene gave the characteristic pinkish-purple coloration which preserved its intensity throughout the experiment, it is clear that iodine is absorbed by the solution of tetraphenyldiphenoxyethane. It is difficult, however, to employ exact titrational methods owing to the indefiniteness of the colour changes and the necessity for carrying out the experiment rapidly to avoid undue thermal decomposition of the material.

For the purpose of ascertaining whether substitution of any kind occurs on the addition of iodine, the following experiment was carried out with the non-dissociating diphenyldiphenoxymethane. A xylene solution of the substance of approximately the same concentration as that employed in the case of tetraphenyldiphenoxyethane was treated with 0·05N-iodine solution in the manner previously described. It was found, however, that the addition of 0·2 c.c. of iodine solution produced a pinkish-purple coloration, which showed no decrease in intensity after 2 hours at 110°.

It appears, therefore, that the absorption of iodine by hot solutions of tetraphenyldiphenoxyethane is due to the direct addition to the unsaturated diphenyldiphenoxymethyl radical. Whereas hexaphenylethane absorbs 80% of the theoretical amount of iodine at ordinary temperature, the absorption of halogen by tetraphenyldiphenoxyethane at 110° is only 28·5%.

Isomerisation in Presence of Hydrogen Chloride.—Since hexaphenylethane undergoes rapid isomerisation to *p*-benzhydryltetraphenylmethane in the presence of hydrogen chloride, we examined the possibility of the formation of a similar compound, $CPh_2(OPh)\cdot C_6H_4\cdot CH(OPh)Ph$, from tetraphenyldiphenoxyethane. A nearly saturated solution of the latter (0·5 g.) in benzene was treated with 12 c.c. of a cold, saturated solution of hydrogen chloride in the same solvent. After standing for 36 hours in a sealed vessel, the solution was concentrated under reduced pressure in a stream of carbon dioxide; the dark oily residue did not contain a chloride of the triphenylmethyl chloride type, since it gave no coloration with an ethereal solution of mercuric chloride.

Irradiation of Tetraphenyldiphenoxyethane.—A 2·5% solution of tetraphenyldiphenoxyethane in benzene in a sealed glass tube was exposed to direct sunlight for 3 weeks. After removal of the benzene under reduced pressure in a stream of carbon dioxide, practically the whole of the compound was recovered unchanged. Its photochemical stability is thus much higher than that of hexaphenylethane, which suffers rapid and complete decomposition under these conditions.

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