CXLVI.—*The Photodecomposition of Triphenylmethyl.*

By SYDNEY THOMAS BOWDEN and WILLIAM JACOB JONES.

THE decolorisation of the free radical triphenylmethyl in direct sunlight was discovered by Gomberg and Cone (*Ber.*, 1904, **37**, 3545), who obtained as products of the reaction in benzene solution triphenylmethane, an oil, and at least two different solid substances. According to these investigators, photochemical decomposition in carbon tetrachloride solution proceeds much more rapidly than in benzene and takes a different course, an oil and a mixture of crystalline substances, but no triphenylmethane, being formed. They state that in diffused light solutions of triphenylmethyl suffer only traces of decomposition, even after being kept for longer than a year.

Schmidlin and García-Banús (*Ber.*, 1912, **45**, 1344) observed rapid and complete decolorisation of benzene solutions of the free radical even in diffused daylight, but only when the solution was optically pure and prepared in the cold by the action of molecular silver on triphenylchloromethane. The application of heat and the use of less noble metals gave yellow impurities, which were more stable in the light and masked the decolorisation of the free-radical solutions. It was in this manner that Schmidlin and García-Banús explained the contradiction between their observations and those of Gomberg and Cone; moreover, they showed that, under the action of light, triphenylmethyl in benzene solution decomposed quantitatively into triphenylmethane and diphenylbisdiphenylene-ethane.

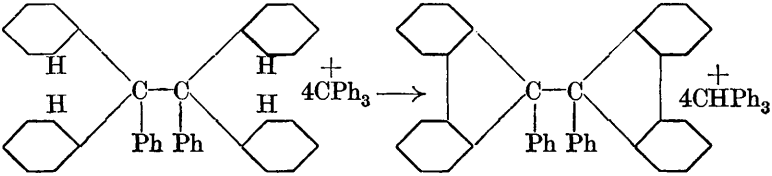
The present investigation was undertaken (*a*) to ascertain whether ultra-violet light is active in effecting autoxidation and reduction of triphenylmethyl, (*b*) to determine the effective region of the visible spectrum in causing photodecomposition, and (*c*) to examine the behaviour of the free radical in various solvents.

We have found that in ultra-violet light triphenylmethyl does not undergo appreciable autoxidation and reduction, either in the solid state or in solution in benzene. Furthermore, an irradiated system in which triphenylmethyl is being prepared by the agitation of mercury with a benzene solution of triphenylchloromethane gives the same characteristic yellow solution as a similar system which is not irradiated. We find also, in accordance with the results of Schmidlin and García-Banús, that solutions of triphenylmethyl are completely decolorised even in diffused daylight, and deposit crystals of diphenylbisdiphenylene-ethane. The decolorisation is observed to be complete even when mercury is employed in the preparation of the free radical. Moreover, a benzene solution of triphenylmethyl, prepared directly by agitating together pure mercury, benzene, and triphenylchloromethane (without previous isolation of the solid free radical), is similarly completely decolorised on exposure to sunlight. It would appear, therefore, that the cause of the contradiction between the observations of Gomberg and Cone and those of Schmidlin and García-Banús is to be referred to the different intensities of light to which their respective preparations were exposed. In this connexion it is evident that the rate of photodecomposition in diffused light is considerably less than that which obtains in direct sunlight, for in diffused light of low intensity, solutions of triphenylmethyl may be kept for several months without giving perceptible indication of loss in colour.

It has been ascertained that the region of the visible spectrum which is most active in effecting the photodecomposition is the green-blue, *viz.*, 5300—4000 Å.U. It is in this region that triphenylmethyl exhibits strongest absorption (Meyer and Wieland, *Ber.*, 1911, **44**, 2557), so that, in this case, it is the region of greatest absorption which is the most photochemically active. In yellow light triphenylmethyl does not undergo autoxidation and reduction. In this connexion it may be mentioned that Luther and Plotnikoff (*Z. physikal. Chem.*, 1908, **61**, 524) showed that in the oxidation of hydriodic acid by oxygen, the blue region of the spectrum is most active, and that the ultra-violet rays are comparatively ineffective.

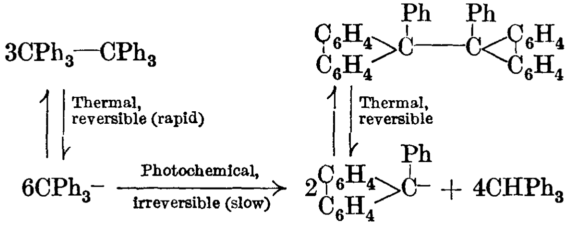
The exposure of 2% triphenylmethyl solutions to direct sunlight (in April) results in their complete decolorisation in about 3 hours, and in the subsequent deposition of crystals of diphenylbisdiphenylene-ethane. Very frequently deposition of the latter compound occurs before the solution is completely decolorised. When the solution of the free radical is agitated during exposure, decolorisation naturally proceeds more rapidly, owing to the fact that fresh layers of the solution are exposed to the light. The presence of triphenylmethyl peroxide or triphenylchloromethane causes no change either in the course or in the products of the reaction.

Schmidlin and García-Banús (*loc. cit.*) regard the easily dissociated hexaphenylethane as being oxidised by the triphenylmethyl to the difficultly dissociated diphenylbisdiphenylene-ethane, and formulate the photochemical change as follows :



On the basis that the valences of the atoms in the triphenylmethyl complex possess different polarities, Fry (*Z. physikal. Chem.*, 1915, **90**, 458) has given a specific interpretation of this reaction in terms of the electronic conception of positive and negative valences.

The chemical and physical properties of solutions of hexaphenylethane are most readily explained on the Gomberg theory, which postulates the dissociation and isomerisation of the fully saturated hydrocarbon. In view of this, it becomes of interest to inquire into the reaction mechanism of the photodecomposition. In benzene at the temperature of the irradiation experiments, the degree of dissociation of the hexa-arylethane, and consequently, the amount of unimolecular form present, is of low order. However, the extreme mobility of equilibration is shown by the marked reactivity of the solutions, for under ordinary conditions the main constituent of the solution is the bimolecular form. Inasmuch as it is improbable that irradiation of the system will influence materially the degree of dissociation of the bimolecular form, it would appear that the photochemical reaction is to be regarded as occurring in the first place between the products of thermal dissociation. Furthermore, in view of the fact that the photochemical change involving the unimolecular forms proceeds considerably more slowly than the equilibration of the system, it follows that the former reaction will determine the measured rate of photodecomposition. One of the final products of the reaction, *viz.*, diphenylbisdiphenylene-ethane, is likewise slightly dissociated in solution. On the assumption that the first product of photochemical change is phenyldiphenylenemethyl, which subsequently undergoes association to the corresponding bimolecular form, the complete scheme for the photochemical autoxidation and reduction of hexaphenylethane solutions may be represented as follows :



For simplicity of representation, no distinction is made in the above scheme between the benzenoid and the quinonoid forms, but on the assumption that both forms are photosensitive to a particular range of frequencies it is extremely improbable that they will be photosensitive to the same degree. Under these conditions, the irradiation of a system containing hexaphenylethane effects the photochemical transformation of one or both types of radicals into phenyldiphenylenemethyl and triphenylmethane. As a result, simultaneous dissociation of the bimolecular hexaphenylethane and association of phenyldiphenylenemethyl to diphenylbisdiphenylene-ethane occurs, so that complete transformation of the first into the last two is ultimately realised. Inasmuch as there are present two types of " odd " molecules, *viz.*, triphenylmethyl and phenyldiphenylenemethyl, the possibility of inter-association of these two radicals to give the mixed bimolecular form, $CPh_3{-}CPh{<}\begin{matrix}C_6H_4\\ C_6H_4\end{matrix}$, has to be considered. Since the final products of the reaction are diphenylbisdiphenylene-ethane and triphenylmethane, it follows that the mixed form does not have a stable existence under the conditions of the experiment.

The nature of the solvent is found to exert a marked influence on the rate of decolorisation. In the case of non-ionising solvents we find that photochemical change proceeds in all such solvents investigated. On exposing 2% solutions of triphenylmethyl in benzene, toluene, *m*-xylene, mesitylene, and hexane to direct sunlight, decolorisation is observed to be most rapid in hexane. The decolorisation proceeds rapidly in mesitylene also, whereas in *m*-xylene and in toluene the rate of loss in colour is slower, but still more rapid than in benzene.

The photochemical behaviour of triphenylmethyl in a comparatively weakly ionising solvent, such as liquid sulphur dioxide, is entirely different from that in the ordinary non-ionising solvents. When solutions of triphenylmethyl in sulphur dioxide are exposed to light, no indication of photochemical autoxidation is observed. There is no loss in colour after several hours' exposure to sunlight. Furthermore, on exposure to light there is no appreciable change in the conductivity of the solution. This points to the fact that the state of triphenylmethyl in a dissociating solvent is essentially of different character from that existing in non-ionising media.

Although hexaphenylethane in non-ionising solvents exhibits no appreciable conductivity, it has been shown by Walden (*Z. physikal. Chem.*, 1903, **43**, 385) and by Gomberg and Cone (*Ber.*, 1904, **37**, 2043) to behave as an electrolyte in liquid sulphur dioxide. Moreover, the absorption spectrum of triphenylmethyl in non-ionising solvents is different from that in liquid sulphur dioxide (Meyer and Wieland, *Ber.*, 1911, **44**, 2557). The several theories which have been advanced to explain the conductance of triphenylmethyl in sulphur dioxide can also be applied in a general way to account for the photochemical inactivity of the compound in this solvent. At the present time none of these theories is entirely satisfactory. Consideration of the stability of the possible molecular complexes formed between triphenylmethyl and the solvent leads to the conclusion that the photochemical behaviour cannot be materially influenced in this connexion. In the case of sulphur dioxide solutions, if we assume a direct solvation of hexaphenylethane, it is probable that such a solvate would not differ greatly in photochemical behaviour from that of the addition complexes present in the ordinary organic solvents. The complete inhibition of the reaction must be due to the absence of the triphenylmethyl radical in equilibrium with hexaphenylethane. In any case, the photochemical behaviour of the free radical is shown to be entirely different from that of the triphenylmethyl ion, whether the latter be solvated or otherwise.

Even in the solid state, hexaphenylethane gives indications of being photosensitive. Although no change in melting point is observed when the substance is exposed to direct sunlight for several days, a slight loss in colour occurs. It is probable, however, that this is due to the presence of slight traces of adsorbed solvent.

EXPERIMENTAL.

Preparation of Triphenylmethyl.—Preliminary experiments carried out to ascertain the most suitable method of preparing triphenylmethyl showed that the method of Schlenk, Weickel, and Herzenstein (*Annalen*, 1909, **372**, 2) was unsuitable, owing to the relatively high temperature required for the complete reduction of triphenylchloromethane by means of copper. The method of Schmidlin (*Ber.*, 1908, **41**, 423), which depends upon the interaction of magnesium triphenylmethyl chloride with triphenylchloromethane, was found to be far more convenient, but gave a product of uncertain purity owing to contamination with magnesium compounds. The method of Gomberg (*J. Amer. Chem. Soc.*, 1917, **39**, 1652; *Chemical Reviews*, 1924, **1**, 99) proved essentially suitable, but, owing to the possible sensitivity of the photochemical reaction under study to the presence of small amounts of impurities, we made the following modifications : (*a*) The reduction of the triphenylchloromethane to triphenylmethyl was effected in an all-glass vessel, from which the transfer of the solution to the concentrating apparatus took place out of contact with air; (*b*) the solution was filtered prior to concentration; (*c*) the removal of adherent solvent in the later stage of the preparation was carried out by the use of a heating bath of methyl alcohol vapour. Contact of the free radical solution with the stopcocks of the concentrating apparatus was minimised by a suitable device, and intrusion of air into the apparatus during the process of concentration under reduced pressure was effectively prevented by surrounding the top and bottom of the stopcocks with large rubber caps maintained inflated with carbon dioxide.

The carbon dioxide, which provided the inert atmosphere in all the experiments, was rigorously purified, and freed from traces of admixed oxygen by preliminary passage through a solution of triphenylmethyl in benzene. The calcium chloride used for drying the gas was recrystallised in an atmosphere of carbon dioxide, and then dehydrated in a stream of the same gas in order to effect complete removal of occluded oxygen. The acetone employed for crystallising the free radical was prepared in the pure state by the decomposition of its compound with sodium iodide (Shipsey and Werner, J., 1913, **103**, 1255), followed by dehydration and fractionation.

The solid free radical was deprived of traces of solvent in an apparatus designed to prevent undue local heating of the substance, and consisting of a long tube, closed at both ends with rubber stoppers, through which passed short exit tubes provided with stopcocks; one end of the tube was connected to the carbon dioxide generator, and the other to a suction pump and manometer. The long tube was surrounded by a jacket through which the vapour of boiling methyl alcohol was circulated. In this manner, the substance, contained in a porcelain boat placed in the inner long tube, was subjected to a process of solvent removal under reduced pressure in a slow stream of carbon dioxide at a temperature slightly below the boiling point of methyl alcohol.

Irradiation Experiments with Ultra-violet Light.—For the investigation of the action of ultra-violet light on triphenylmethyl in the solid state, the material was contained in a small quartz vessel, and exposed for 5 hours to ultra-violet light from a carbon arc lamp provided with a quartz window: it presented no change in appearance or in melting point after the exposure.

Irradiation of the triphenylmethyl solutions was carried out in specially constructed quartz tubes. The apparatus employed for filling the tubes with solution enabled the operation to be conducted in the entire absence of air. In view of the extremely reactive nature of the radical, it was considered important to avoid contact of the solution with any contaminating surface during the exposure, and accordingly the quartz tubes were sealed off under reduced pressure in the oxy–coal-gas flame. The tubes, which had an approximately elliptical cross-section of long major axis, were closed at the bottom and provided with long, narrow constrictions. The sealing of the tubes was effected at a point sufficiently distant from the liquid surface to prevent undue heating of the solution. This precaution is necessary since triphenylmethyl solutions decompose on excessive heating (Wieland, *Annalen*, 1911, **381**, 200). Care was taken to remove the film of triphenylmethyl solution adhering to the constriction by washing it down several times with pure solvent prior to sealing, and the possibility of contamination of the solution with traces of the thermal-decomposition products of triphenylmethyl was thus avoided. The tubes were exposed with both their longitudinal axes and their longer cross-sectional axes at right angles to the direction of the ultraviolet radiation from a Cooper–Hewitt mercury lamp of fused quartz. The irradiation chamber in which the tubes were placed was cooled by currents of cold air, so that its temperature did not exceed 19°. After 60 hours' intermittent exposure to the ultraviolet radiation, the solution presented no change in appearance, and no perceptible decrease in the intensity of the characteristic yellow colour was observed on comparison with a control solution of the same concentration which had not been irradiated. A solution of triphenylmethyl containing, in the first instance, traces of oxygen likewise showed no loss in colour on exposure to ultra-violet light for 15 hours.

In order to ascertain whether autoxidation and reduction of triphenylmethyl in ultra-violet light took place during its formation from triphenylchloromethane, a 6% solution of the aryl chloride in benzene was introduced into a quartz tube of the form already described; excess of pure air-free mercury was added, and the tube sealed. A control solution of the same concentration, together with the same amount of mercury, was also prepared and suitably protected from ultra-violet light. Both tubes were attached to a shaking machine, which effected gentle agitation of the contents whilst the arrangement was exposed to ultra-violet light from the mercury lamp. As agitation proceeded, a slight yellow colour appeared, together with a small amount of mercurous chloride; further agitation produced a continuous deepening in colour. The yellow colour so obtained was identical with that produced in the case of the solution which had been protected from ultra-violet light. Furthermore, on removing the solutions from the tubes and allowing them to stand in the air for a short time, impure triphenylmethyl peroxide, m. p. 179°, was obtained.

The progressive generation of the characteristic yellow colour of triphenylmethyl under the above conditions affords additional confirmation of the observations made upon the specially prepared solutions of the radical. In neither case is decolorisation of the solution evident, and there is no formation of diphenylbisdiphenylene-ethane. However, a solution of triphenylmethyl of the same concentration in benzene, and prepared from the same sample of the radical, when exposed to direct sunlight gave full decolorisation in less than 3 hours, together with a quantitative yield of white crystals of diphenylbisdiphenylene-ethane.

It is to be concluded, therefore, that autoxidation and reduction of triphenylmethyl is not produced by ultra-violet radiation, and the actinic power of these rays for this particular photochemical reaction is of low order.

The Chemical Effect of the Visible Spectrum.—An experiment, in which the illumination was provided by 60-c.p. electric lamps in conjunction with Wratten filters of known wave-length transmission, was not successful, and after a period of 4 weeks the change in colour of triphenylmethyl solutions thus illuminated was imperceptible. Furthermore, the change in colour produced in dilute benzene solutions of triphenylmethyl during 4 weeks' direct exposure to light from the above source was extremely slight, so that the free radical can be prepared with perfect safety in a room illuminated by ordinary filament electric lamps.

By employing solutions of dyes as light filters, conclusive results were obtained in direct sunlight, and the region of the visible spectrum which produced photodecomposition of triphenylmethyl was in this manner definitely established. The following solutions of water-soluble dyes were employed: Tartrazine (1 in 1,000), Congo-red (1 in 28,000), naphthol-green (1 in 6,000), methyleneblue (1 in 60,000), and crystal-violet (1 in 105,000). Tubes containing identical solutions of triphenylmethyl were symmetrically immersed in larger concentric tubes containing the respective dye solutions, and provision was made for the equal illumination of the systems. Exposure of the tubes to direct sunlight for 20 minutes indicated that decolorisation occurred most rapidly under green, blue, and violet light. Complete decolorisation first took place under blue illumination, whereas the solution of triphenylmethyl under red illumination was only slightly decolorised. Under yellow light, the free-radical solutions showed only slight indications of loss in colour even after several hours' exposure.

These observations indicate that the blue-green region of the spectrum is most active in effecting the photodecomposition of triphenylmethyl in benzene solution.

The Effect of the Solvent.—The nature of the solvent was found to exert a pronounced influence on the course of the photochemical reaction. As representative of non-ionising solvents we employed benzene, toluene, *m*-xylene, mesitylene, and hexane. All the solvents were carefully purified, and subjected to a final fractionation immediately before use.

2% Solutions of triphenylmethyl in each of the above solvents were introduced into the specially prepared tubes, the operations being conducted in the entire absence of air by means of the apparatus previously described. The sealed tubes were exposed at the same temperature to direct sunlight, and the respective rates of decolorisation observed by comparison with control tubes kept in the dark. Striking differences in the rates were shown by the different solutions. In toluene, decolorisation was more rapid than in benzene, in mesitylene and *m*-xylene solutions it was even faster, and in hexane most rapid of all.

Similar results were obtained when the above experiments were repeated in diffused light.

Sulphur dioxide solutions. The investigation of the behaviour of triphenylmethyl in an ionising medium naturally resolves itself into a study of the triphenylmethyl ions, either free or solvated, as distinct from that of the uncharged forms which exist in the usual non-ionising organic solvents. For our immediate purposes, sulphur dioxide appeared to be the most suitable ionising solvent. The experimental procedure differed in minor details from that adopted in the case of the preceding organic solvents, inasmuch as special provision had to be made for the preparation of standard solutions of triphenylmethyl in a low-boiling solvent of this nature.

The gas was dried by passage through a long tube containing phosphoric oxide, and was then led to the experimental tube immersed in a freezing mixture preserved in a Dewar flask. The tube, provided with a long constriction, was previously charged with a known weight of triphenylmethyl, and after the condensation of the required volume of sulphur dioxide, the tube was sealed at the constriction by means of a blowpipe flame. 0·5% and 1% Solutions were prepared in this manner, and each solution was exposed to direct sunlight and its behaviour compared with that of a benzene solution of the same concentration. Although the benzene solution underwent rapid decolorisation in the manner previously described, no perceptible loss in colour took place in the case of the sulphur dioxide solutions.

In view of the fact that these colorimetric experiments gave no indication of photochemical autoxidation, further experiments were carried out in which the solution was exposed to sunlight in an electrolytic conductivity vessel consisting of a long tube provided with two platinum electrodes. The cell was charged with a solution of triphenylmethyl in accordance with the procedure previously indicated, and then sealed. The conductances of the solution determined at 18·5° in the dark and in sunlight showed no appreciable difference.

Action of Light on "Solid Triphenylmethyl."—The action of direct sunlight on so-called solid triphenylmethyl was investigated by sealing the finely-powdered material in thin-walled capillary tubes in an atmosphere of carbon dioxide. When exposed to sunlight for several days, the substance was found to be very slightly paler in colour, although the melting point was unchanged in comparison with samples of the same material which had throughout been protected from light. Further experiments carried out with the substance contained in tubes which were highly evacuated before sealing gave similar results.

The photochemical change in the solid state is thus of low order, and is probably due to the presence of a small amount of adsorbed solvent, since it is difficult to remove entirely the last traces of solvent even by maintaining the substance at 66° under a pressure of 15 mm.

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