

The Ultraviolet Photochemistry of Derivatives of Triphenylmethane

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HALFORD¹ showed that solutions of triphenylmethyl bromide in cyclohexane on irradiation with ultraviolet light gave rise to triphenylmethyl free-radicals (I) which reacted with oxygen to form triphenylmethyl peroxide. In the absence of oxygen, radicals produced by the dissociation of hexaphenylethane have been shown² to undergo disproportionation by hydrogen exchange to form triphenylmethane (II) and the 9-phenylfluorenyl free-radical which could gain a hydrogen atom to form 9-phenylfluorene (III) or dimerise to 9,9'-diphenylbifluorenyl (IV). One mechanism, proposed² to account for the formation of (II) and (III) when the solvent was alkaline dioxan, involved (I) in an excited electronic state. More recently, Kozlov³ has produced (I) by photolysis of $(C_6H_5)_3C-X$ (where $X = H, OH, \text{ or } Cl$) in ethanol at 77°K. We present here a preliminary account of an investigation into the primary processes of

are given in the Table. In Letsinger's experiments using alkaline dioxan as solvent, the formation of (III) would be favoured at the expense of (II).

Rigorously outgassed solutions of (V) in quartz spectrophotometer cells were irradiated and the reaction was followed by measuring the optical density at 261 $m\mu$. The overall change in optical density at 261 $m\mu$ was that expected from the conversion of (V) into 90% of (II) and 10% of (III) assuming that these were the only products formed. Since the molar extinction coefficients of (V), (II), and (III) at 261 $m\mu$ are 1.75×10^3 , 0.83×10^3 , and 16.9×10^3 respectively, the increase in optical density at 261 $m\mu$ was mainly due to the formation of (III). Assuming that (II) and (III) were the only products, relative rates of formation of 9-phenylfluorene and of the composition of the products were calculated.

The quantum yield of appearance of (III) was

TABLE

Initial concentration of (V) (moles l. ⁻¹)	% Reaction	Triphenylmethane (II)	Percentage yields 9-Phenylfluorene (III)	9,9'-Diphenylbifluorenyl (IV)
1.04×10^{-2}	~85	52.0	16.0	10.0
4.88×10^{-4}	~85	68.7	17.5	0
4.0×10^{-4}	~85	70.1	15.0	2.1
Letsinger*	—	31.7	45.0	—

*Ref. 2. Yield calculated as a percentage of twice the concentration of hexaphenylethane.

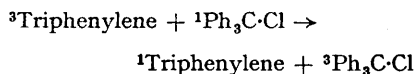
the ultraviolet photolysis of solutions of triphenylmethyl chloride (V) in cyclohexane at room temperature in the absence of oxygen.

In a quantitative analysis of the products of the reaction, solutions of (V) in cyclohexane which had been rigorously outgassed were irradiated by the unfiltered light from a Hanovia medium-pressure mercury arc. The products were separated by preparative thin-layer chromatography and the yields together with those of Letsinger²

independent of the concentration of (V) over the range 10^{-5} — $2 \times 10^{-4}M$ when the light intensity was kept constant. When the concentration of (V) was kept constant and the light intensity varied the initial rate of reaction was directly proportional to the intensity of the absorbed light.

In order to determine whether the triplet excited state of (V) was involved in the reaction, the effect of a known⁴ triplet sensitiser (triphenylene) on the initial rate of the reaction was investigated

and the results are shown in Figure 1, curve A. The increase in the initial rate was directly proportional to the concentration of triphenylene added. The composition of the products as calculated from the change in optical density depended on the concentration of triphenylene added (Figure 1, curve B) but the final spectrum showed the unchanged characteristic structure of triphenylene. This suggested that the triphenylene remained unchanged during the reaction but increased the relative amount of 9-phenylfluorene formed at the expense of the methane. The triphenylene sensitised the reaction by a process of the type:—



since Hammond⁴ has shown that singlet triphenylene undergoes intersystem crossing to triplet triphenylene with 95% efficiency. Acetophenone also affected the rate of the reaction in the same way.

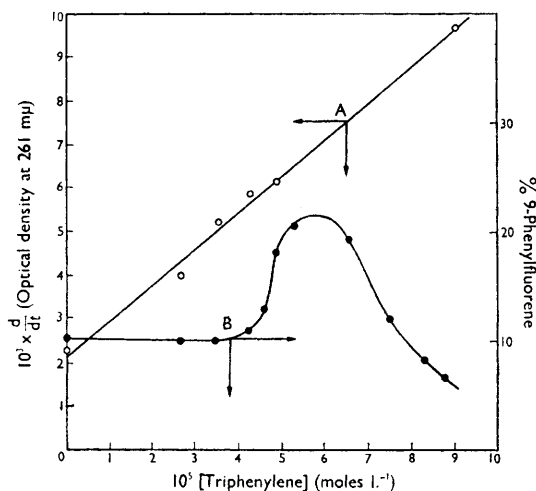
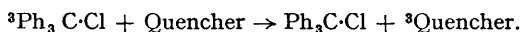


FIGURE 1

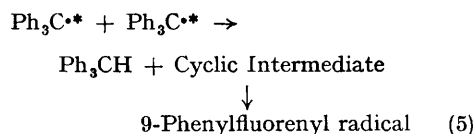
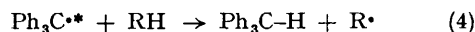
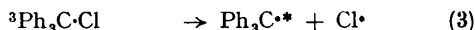
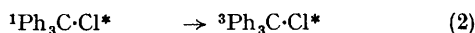
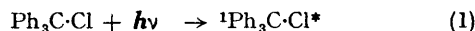
The addition of substances having lower-lying triplet levels than (V) would be expected to quench the reaction of (V) by a reaction:—



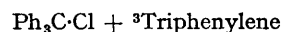
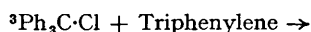
Both anthracene and azulene did have a quenching effect which was small in both cases. Since the concentrations of quenchers had to be

kept small to prevent the possibility of an inner filter effect, only a small quenching effect was expected. The results of adding triplet-state sensitizers and quenchers provided a strong indication that the triplet state of (V) was involved in the photolysis.

The primary processes of the photolysis may be described by a mechanism the essential steps of which are:—



The formation of 9-phenylfluorene by Reaction 5 is a mechanism which has been proposed² in which a hydrogen atom transfer takes place from one triphenylmethyl radical to another. The triphenylmethane can thus be formed in two ways (a) by Reaction 4, a process involving only one triphenylmethyl radical and (b) by Reaction 5 which involves two triphenylmethyl radicals. The second process also forms a molecule of 9-phenylfluorene. Any factors which increase the concentration of (I) would therefore have a greater effect on Reaction 5 than Reaction 4 and would increase the amount of (III). The addition of triphenylene therefore by increasing the concentration of (I) increases the proportion of 9-phenylfluorene formed. This increase would reach a maximum with increasing concentration of triphenylene (Figure 1, curve B) since with increasing concentration, as well as sensitising the formation of triplet (V), triphenylene would have a concentration quenching effect. It could also quench by a process of the type:—



since Sandros⁶ has shown that transfer of triplet-state energies may be reversible when the energies of donor and acceptor are matched.

The difference between the relative amounts of products obtained from the large-scale photolyses and those calculated on the basis of the change in optical density may also be due to the relative importance of Reactions 4 and 5. Since the large-scale runs were taken to only 85% of reaction the

remaining 15% would be expected to lead almost exclusively to the formation of (II). In our less alkaline solvent the allylic shift of hydrogen suggested by Letsinger would be more difficult and so (II) would be more likely to be formed by hydrogen abstraction from the solvent. The participation of the solvent in Reaction 4 is

confirmed by the isolation of cyclohexyl hydroperoxide.⁵

The ease with which intersystem crossing (Reaction 2) appears to occur in the absence of a photosensitizer is probably due to the presence of the "heavy" chlorine atom.

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⁵ C. Walling and S. A. Buckler, *J. Amer. Chem. Soc.*, 1955, **77**, 6032.

⁶ K. Sandros and H. L. J. Bäckström, *Acta Chem. Scand.*, 1962, **16**, 958.