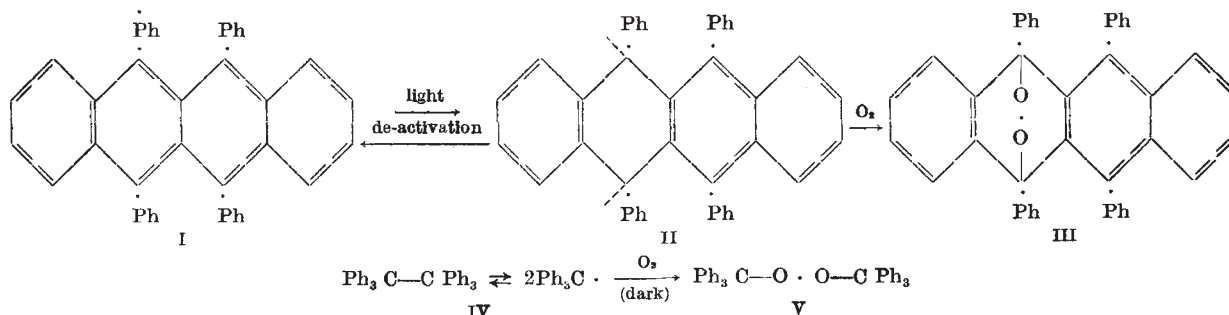


## LETTERS TO THE EDITORS

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### Demonstrability of the Photochemical Formation of Biradicals by Magnetic Methods

THE red 5,6,11,12-tetraphenylnaphthacene (rubrene) (I) is stable to oxygen in the solid state; its solutions, however, are only stable in the dark. When they are irradiated with sunlight or artificial light in the presence of oxygen, a crystalline peroxide (III) is formed<sup>1</sup> (the quantum efficiency of the formation of (III)<sup>2</sup> rises to unity at concentrations greater than 0.01 molar and is independent of wave-length between 3660 and 5460 Å.). The easy formation of this peroxide is reminiscent of the formation of (V) from solutions containing hexaphenylethane molecules, as well as their dissociation products, namely, the paramagnetic triphenylmethyl radicals (IV). (The schemes  $\text{II} \xrightarrow{\text{O}_2} \text{III}$  and  $\text{IV} \xrightarrow{\text{O}_2} \text{V}$  are simplified ones and show in both cases only the initial and final products.)



It has been assumed<sup>3</sup> that light energy transforms the ordinary form of rubrene (I) into a biradical (II), an analogue of triphenylmethyl; it is believed that (II), which should be paramagnetic according to this hypothesis, is able to return to the non-activated diamagnetic state by re-arrangement of the electrons (II  $\rightarrow$  I).

It has been repeatedly stated that the hypothesis of the photoformation of (II) has not been confirmed or has even been contradicted<sup>4</sup> by magnetic measurements, and the criticism is based on Müller's work<sup>5</sup>. According to him, irradiated and non-irradiated solutions of rubrene do not differ in their magnetic properties. No details have been published concerning the photo-experiments, for example, the intensity and nature of the light used in the experiment.

Müller's experiments can, however, scarcely be accepted as evidence against the formation of (III) via a biradical mechanism (comp. II), as the following calculations show that it is very difficult to detect the photochemical formation of activated paramagnetic molecules, in consequence of their low concentration, by the method applied by Müller.

Let  $q$  denote the rate of the photo-activation process  $\text{I} \rightarrow \text{II}$ ,  $x$  the number of activated molecules (radicals) II present at a given time, both  $q$  and  $x$  expressed as fractions of the total number of molecules (I). Denote by  $\tau$  the life-time of a radical (II) before returning to (I); then  $1/\tau$  is the probability of deactivation  $\text{II} \rightarrow \text{I}$  per unit time. One has for the reaction velocity the equation

$$\frac{dx}{dt} = -\frac{x}{\tau} + q,$$

the solution of which satisfying the initial condition  $x(0) = 0$  is

$$x = q\tau \{1 - \exp(-t/\tau)\}.$$

It tends to the stationary state  $x = q\tau$ .

One can estimate that with the sources available for these experiments (300-watt lamp) the number of photons absorbed is about  $10^9$  per second per mole; hence, as only part of these photons are used for activation, one has  $q < 10^{-4}$  sec<sup>-1</sup>. Hence  $\tau > 10^4 x$  sec.

The sensitivity for discovering magnetic radicals ought to be, therefore, better than  $x \sim 10^{-4}$  in order to have the lower limit of  $\tau$  of the order of 1 sec. It is not very likely that life-times of diradicals produced by photo-activation are so long. With the Curie balance the limit of detection is about 1 per cent,  $x = 10^{-2}$ , hence  $\tau > 100$  sec. A life-time of this length would be observable by the retardation of the establishment of equilibrium. In fact, no such time-lag has been observed.

The extremely low concentration of the photo-activated molecules is not inconsistent with the fact

that (III) is formed rather rapidly; activated molecules which disappear from the photo-equilibrium (I  $\rightleftharpoons$  II) in consequence of de-activation or peroxide formation are replaced almost instantaneously; the disadvantage of the low concentration of the activated molecules is counterbalanced by their rapid reformation.

It is hoped that, by the application of a more sensitive method (magnetic resonance may be tried) such as the one used by Müller, the question whether photo-activated organic molecules may be paramagnetic in spite of the fact that the non-activated form is diamagnetic will be solved. This question is also important in connexion with the problem of photo-sensitization<sup>6</sup>.

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<sup>1</sup> Moureu, Dufraisse and Dean, *C.R. Acad. Sci., Paris*, **182**, 1440, 1584 (1926). Moureu, Dufraisse and Girard, *ibid.*, **186**, 1027 (1928).

<sup>2</sup> Comp. Bowen and Steadman, *J. Chem. Soc.*, 1098 (1934).

<sup>3</sup> Schönberg, *Ber.*, **67**, 633, 1404 (1934); *Liebig's Ann.*, **518**, 299 (1935); *Trans. Farad. Soc.*, **32**, 514 (1936). Dufraisse, *Ber.*, **67**, 1021, 2018 (1934).

<sup>4</sup> Gilman, "Organic Chemistry", 603 (2nd edit., 1942). Richter-Anschütz, "Chemie der Kohlenstoffverbindungen", **2**, Pt. II, 651 (12th edit., 1935).

<sup>5</sup> Müller, *Z. Electrochem.*, **40**, 512 (1934). Comp. also Müller and Müller-Rodloff, *Liebig's Ann.*, **517**, 134 (1925). They state that they are unable to answer the question whether, in illuminated solutions of rubrene, small amounts of the biradical are present.

<sup>6</sup> Schönberg, *Liebig's Ann.*, **518**, 299 (1935).