Tetrahedron Letters No.55, pp. 4859-4862, 1969. Pergamon Press. Printed in Great Britain.

PHOTOCHEMISTRY OF AROMATIC COMPOUNDS.2.
THE UNUSUAL BEHAVIOUR OF 9,9'-BIFLUORENYLIDENE ON PHOTOREDUCTION[1]

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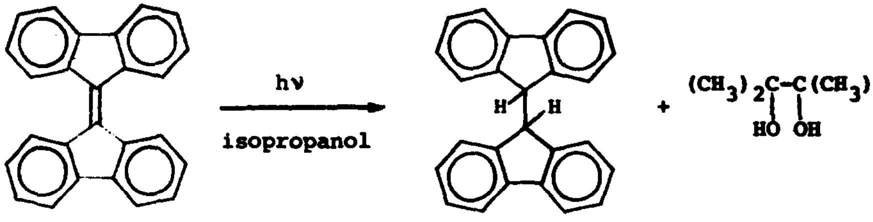
Received in the U K 3 October 1969; accepted for publication 27 October 1969

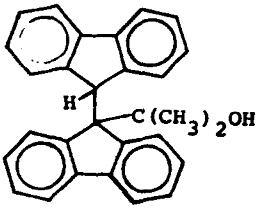
Due to fast internal conversion and vibrational relaxation in excited states, quantum yields of photoreactions of aromatic compounds in solution are usually wavelength independent[2]. The photoreduction of 9,9'-bifluorenylidene (A) in hydrogen donor solvents is abnormal in this respect[3], and we report here the mechanism of this reaction which is dependent on the excitation wavelength.



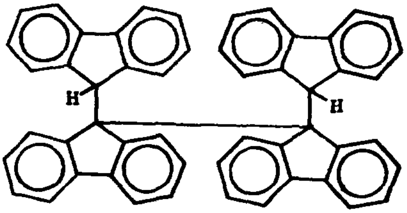
A

AH_2

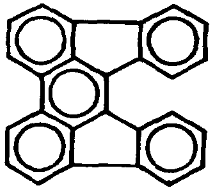
The photoreduction -which can be performed in methanol, ethanol, isopropanol or acetone, but not in benzene- leads exclusively to 9,9'-bifluorene (AH_2) and pinacol when the concentration of A does not exceed 10^{-4}M, in degassed solutions. When the concentration of A is of the order of 10^{-3}M in isopropanol, small amounts of C and D have been isolated, but fluorenofluoranthene (E) was not found[3]. At still higher concentrations, no reaction occurs at all.



C



D



E

A has a strong absorption band in the visible (λ_{max}= 455 nm, ϵ_{max}=$2.2\text{x}10^4$) but in the absence of sensitiser, the reduction takes place only at wavelengths shorter than 315 nm. This appears clearly from figure 1 which shows the concentration of A as a function of time for various conditions.

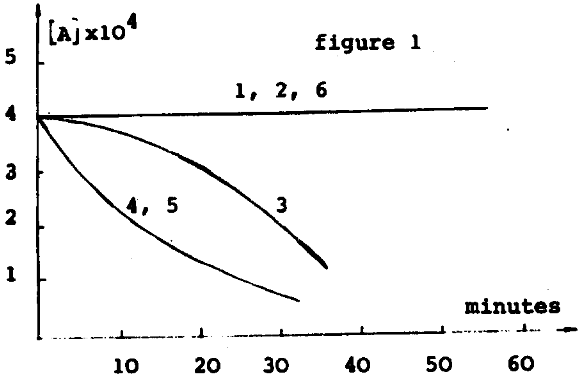


figure 1

N°	Solvent	Excitation wavelength	Sensitiser
1	iPrOH	455 nm	none
2	iPrOH	366 nm	none
3	iPrOH	310 nm	none
4	iPrOH	310 nm	9,9'-bifluorene
5	iPrOH	375 nm	Michler's ketone
6	Benzene	310 nm	none

Comparison of curves 3 and 4 (or 5) illustrates the autocatalytic character of the unsensitised reaction. The short induction period in curve 3 is partly due to traces of oxygen remaining after crude degassing of the samples; in undegassed solutions, the reaction is exceedingly slow[4] and the rate of consumption of A increases steadily when oxygen is removed by nitrogen bubbling. In samples thorougly degassed by freezing-pumping-thawing cycles, the reaction remains however autocatalytic.

It appears then that AH_2 is able to sensitise the reaction (curve 4); this can be understood on the ground of either scheme 1 or 2.

<u>Scheme 1</u>.

$$A^* + AH_2 \longrightarrow 2\,AH\cdot$$

$$AH\cdot \xrightarrow{\text{solvent}} AH_2$$

This scheme was rejected on the ground of the following experiment: A was reduced in the presence of 9,9'-bifluorene specifically dideuterated in positions 9 and 9' (AD_2). The analysis of the reaction mixture by mass spectrometry showed no AHD.

Scheme 2.

$$AH_2^* + A \longrightarrow AH_2 + A^*$$

$$A^* \xrightarrow{\text{solvent}} AH_2$$

AH_2 would act as a sensitiser (λ_{max}= 305 nm) by transfering its energy to A. This agrees well with other sensitisation experiments using Michler's ketone and naphthalene. Although singlet-to-singlet energy transfers are possible on the ground of energy considerations, this type of transfer may be ruled out when the acceptor concentration is as low as 10^{-5}M as in our experiments, taking into account the S_1 state lifetime of the sensitisers used. It appears thus that at least a large part of the photoreduction originates in the triplet manifold.

The phosphorescence spectrum of A has been recorded at 77°K in EPA. The energy of the phosphorescent state is 55.7 kcal/mole, but this slow emission is observed only by excitation at 315 nm or shorter wavelengths. The fluorescence of A is too weak to be observable, and the energy of the 0-0 transition of the S_1-S_0 band was obtained from absorption spectra at liquid nitrogen temperature; it corresponds to an energy of 55.1 kcal/mole. The phosphorescent state is thus at a slightly higher energy than the S_1 state, implying that intersystem crossing from S_1 should be fairly inefficient. This explains why phosphorescence is observed only by excitation to highersinglet states.

There is thus a striking parallelism between the unusual photochemical behaviour and the spectroscopic properties of bifluorenylidene.

The photochemistry of this compound is being investigated further.

Experimental

The U.V. absorption spectra were recorded with a Cary 14 spectrometer. Photochemical reactions were carried out in cylindrical quartz cells of variable pathlengths (1, 2, 5 and 10 cm). The solutions were irradiated using a 250 W high pressure mercury arc in combination with a Baush and Lomb monochromator, spectral distributions at the various wavelengths being checked with a Hilger and Watts Medium quartz spectrograph. The same spectrograph was used to record the phosphorescence spectra.

Acknowledgement. We thank Professor R. H. Martin for his interest, the Fonds National de la Recherche Scientifique (for E.V.D) and the Institut pour l'Encouragement de la Recherche Scientifique dans l'Industrie et l'Agriculture (for M.J.) for fellowships. This work is supported by the Fonds de la Recherche Fondamentale Collective under contract N°621.

References.

1. For part 1, see E. Vander Donckt, R. Dramaix, J. Nasielski, C. Vogels, Trans. Faraday Soc., (in press)
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3. G. P. De Gunst, Rec. Trav. Chim., 88, 801 (1969)
4. The quantum yield for the photo-oxydation to fluorenone has been found to be $4x10^{-4}$ (ref. 3)