Tetrahedron Letters No. 26, pp 2389 - 2392.
© Pergamon Press Ltd. 1979. Printed in Great Britain.

0040-4039/79/0622-2389$02.00/0

PHOTOCHEMISTRY OF CATION RADICALS IN SOLUTION : PHOTOINDUCED OXIDATION BY THE PHENOTHIAZINE CATION RADICAL.

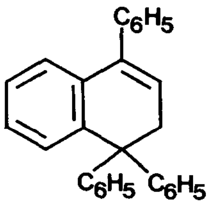
Jean-Claude MOUTET* and Gilbert REVERDY*+

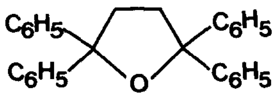
*Laboratoire d'Electrochimie Organique et Analytique (ERA CNRS 675),
Département de Recherche Fondamentale, Centre d'Etudes Nucléaires
de Grenoble, 85X 38041 Grenoble Cedex (France) et +Centre universitaire de Savoie, UER Sciences, BP143 73011 Chambéry Cedex (France).

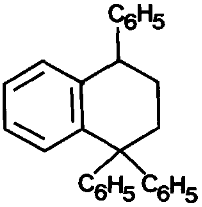
Summary : *Irradiation of phenothiazine cation radical, Ph*$^{\cdot+}$*, with 1,1-diphenylethylene, DPE, causes its reduction to Ph and oxidation of DPE. Cyclodimeric products are formed from DPE*$^{\cdot+}$*.*

The reactivity of cation radicals in solution has been thoroughly studied[1]. Among the principal reactions which they undergo are dimerization, disproportionation, electron transfer and reaction with nucleophiles[1]. However, there is only one detailed report of their photochemical properties in solution by Parker and Svanholm[2], who described the photobenzidine rearrangement of the tetraphenylhydrazine cation radical.

We wish to report the first example of a photoinduced oxidizing property of a cation radical[3]. We find that with 1,1-diphenylethylene, DPE, the phenothiazine cation radical Ph$^{\cdot+}$ excited by visible light is reduced to Ph and initiates a reaction leading from the cation radical DPE$^{\cdot+}$ to the dihydronaphtalene 1 and the tetrahydrofuran 2.


1


2


3

Controlled potential oxidation of Ph (2×10^{-3} M in deoxygenated acetonitrile with $LiClO_4$ 10^{-1} M) at 0.6 V (vs Ag/Ag$^+$ 10^{-2} M) affords the cation radical Ph$^{\cdot+}$. Pt rotating disk voltammetry gives a monoelectronic reduction wave ($E_{1/2} = 0.27$ V)[4]. The absorption spectrum of the solution obtained exhibits an absorption area from 375 to 550 nm with maxima at 516 nm ($\varepsilon_{max} = 6920$) and 438 nm ($\varepsilon_{max} = 4365$), shoulders at 497, 480 and 405 nm and a weaker absorption area from 600 to 1000 nm ($\lambda_{max} = 735$ nm, $\varepsilon_{max} = 1020$). This spectrum is solely due to the phenothiazine cation radical monomer, dissociated from its counter ion[5], namely ClO_4^- which has no absorption in the visible region.

When preparedthis way, Ph$^{\cdot +}$ perchlorate is stable for a few hours upon irradiation with the filtered light $\lambda > 400$ nm from a mercury high-pressure lamp. Upon addition of DPE 3.5×10^{-2} M, there is no evidence of reactivity in the dark. On the other hand, irradiation of this solution with light of wavelengths greater than 400 nm (DPE does not absorb in this region) causes the reduction wave of Ph$^{\cdot +}$ to disappear in a few hours. And at the same time the oxidation wave of Ph and a new reduction wave ($E_{1/2} = -0.2$ V) typical of the release of protons appear. The values of the limiting current of the voltammetry curve after complete disappearance of Ph$^{\cdot +}$ indicate that irradiation causes the complete reduction of the latter back to Ph and the release of an equimolar quantity of protons. In a separate experiment under identical conditions, an amperometric titration using 2,6-lutidine confirmed the appearance of an equivalent of protons per equivalent of Ph produced. Quantitative high pressure liquid chromatography, HPLC, of the irradiated solution showed that for 100 parts of Ph regenerated,50 parts of the cyclodimeric products $\underline{1}$ and $\underline{2}$ (22 parts of $\underline{1}$ and 28 parts of $\underline{2}$) are formed. Then two competitive photoreactions occur. They are described by the following equations :

$$2\ \mathrm{Ph}^{\cdot +} + 2\ \mathrm{DPE} \xrightarrow[\mathrm{CH_3CN}]{h\nu} 2\ \mathrm{Ph} + \underline{1} + 2\ \mathrm{H}^+$$

$$2\ \mathrm{Ph}^{\cdot +} + 2\ \mathrm{DPE} \xrightarrow[\mathrm{CH_3CN}]{h\nu,\ \mathrm{H_2O}} 2\ \mathrm{Ph} + \underline{2} + 2\ \mathrm{H}^+$$

The role of residual water in the formation of $\underline{2}$ becomes obvious when irradiation is carried out in an acetonitrile / trifluoroacetic anhydride solvent mixture[6]. In this case $\underline{2}$ does not appear. Instead, the competitive photochemical reaction goes with substitution reactions on Ph$^{\cdot +}$ in its ground state doubtless by $\mathrm{CF_3CO_2}^-$.

Preparative HPLC of the photolysis medium without $\mathrm{(CF_3CO)_2O}$ allows isolation of traces of 1,1,3,3-tetraphenyl-1 butene $\underline{4}$ (as well as an excess of DPE and the photoproducts Ph, $\underline{1}$ and $\underline{2}$). This is not due to a photochemical process but is obtained by dimerization of DPE[7] through acidification of the solution during photolysis.

The formation of a DPE cyclodimeric product is reminiscent of an observation by Arnold et al.[8] who irradiated a solution of DPE and methyl p-cyanobenzoate, A, in acetonitrile. In this case the transfer of one electron from DPE to A* led, via an exciplex, to the solvated ion radicals DPE$^{\cdot +}$ and A$^{\cdot -}$ (Scheme I). A tetrahydronaphtalene $\underline{3}$ was formed after nucleophilic attack on DPE by DPE$^{\cdot +}$ followed by ring closure of the dimeric cation radical $(\mathrm{DPE_2})^{\cdot +}$, back electron transfer from A$^{\cdot -}$ and aromatization:

$$\mathrm{A}^{*} + \mathrm{DPE} \longrightarrow [\mathrm{A.\ DPE}]^{*} \xrightarrow{\mathrm{CH_3CN}} \mathrm{A}^{\cdot -}_{(\mathrm{solv})} + \mathrm{DPE}^{\cdot +}_{(\mathrm{solv})}$$

$$\mathrm{DPE}^{\cdot +}_{(\mathrm{solv})} \xrightarrow{\mathrm{DPE}} (\mathrm{DPE_2})^{\cdot +}_{(\mathrm{solv})}$$

$$(\mathrm{DPE_2})^{\cdot +}_{(\mathrm{solv})} \xrightarrow[\text{and } \mathrm{A}^{\cdot -}_{(\mathrm{solv})}]{\text{cyclization}} \underline{3} + \mathrm{A}$$

Scheme I

In the present work, we expect a different development of the photochemical sequence if DPE$^{\cdot+}$ and then (DPE$_2$)$^{\cdot+}$ are first formed. In fact, the dimeric cation radical finds itself in a medium which includes Ph$^{\cdot+}$, an oxidant, in contrast with the reported example[8] where it was in a medium including a reductant A$^{\cdot-}$. In scheme II, we propose the reactions (4) and (5) to explain the formation of 1 and 2 from (DPE$_2$)$^{\cdot+}$. In the reaction (4) which involves a cylization, an oxidation by Ph$^{\cdot+}$ and a double deprotonation, it is not presently possible to determine whether cyclization or oxidation occurs first. A possible cyclization of (DPE$_2$)$^{2+}$ must be considered since cyclizations of dimeric dications of p-substituted *trans*-stilbenes are well known[9]. In the case of the reaction (5) we suggest the oxidation of (DPE$_2$)$^{\cdot+}$ to (DPE$_2$)$^{2+}$ by Ph$^{\cdot+}$. This is followed by the attack of water, cyclization and the loss of two protons. Hydrolysis of a dimeric dication has been observed with the formation of a tetrahydrofuran during the electrochemical oxidation of 4,4'-dimethoxystilbene[10].

$$\mathrm{Ph}^{\cdot+}_{(\mathrm{solv})} \xrightarrow[\mathrm{CH_3CN}]{h\nu,\ \lambda\ >\ 400\ \mathrm{nm}} \left(\mathrm{Ph}^{\cdot+}_{(\mathrm{solv})}\right)^{*} \qquad (1)$$

$$\mathrm{DPE} + \left(\mathrm{Ph}^{\cdot+}_{(\mathrm{solv})}\right)^{*} \dashrightarrow \mathrm{DPE}^{\cdot+}_{(\mathrm{solv})} + \mathrm{Ph} \qquad (2)$$

$$\mathrm{DPE}^{\cdot+}_{(\mathrm{solv})} \xrightarrow{\mathrm{DPE}} (\mathrm{DPE}_2)^{\cdot+}_{(\mathrm{solv})} \qquad (3)$$

$$(\mathrm{DPE}_2)^{\cdot+}_{(\mathrm{solv})} \xrightarrow[\text{cyclization}]{\mathrm{Ph}^{\cdot+}_{(\mathrm{solv})}} \underline{1} + \mathrm{Ph} + 2\,\mathrm{H}^{+} \qquad (4)$$

$$(\mathrm{DPE}_2)^{\cdot+}_{(\mathrm{solv})} \xrightarrow[\text{cyclization}]{\mathrm{Ph}^{\cdot+}_{(\mathrm{solv})},\ \mathrm{H_2O}} \underline{2} + \mathrm{Ph} + 2\,\mathrm{H}^{+} \qquad (5)$$

Scheme II

In scheme II, we propose that the excited solvated cation radical $\left(\mathrm{Ph}^{\cdot+}_{(\mathrm{solv})}\right)^{*}$ oxidizes DPE. The study of the absorption spectra of the different compounds (Ph, Ph$^{\cdot+}$, ClO$_4^-$, DPE, 1, 2, 4) included in the medium shows that Ph$^{\cdot+}_{(\mathrm{solv})}$ is the species initially excited. Only Ph$^{\cdot+}_{(\mathrm{solv})}$ absorbs wavelenghts longer than 400 nm. And addition of DPE to the solution does not alter the absorption spectrum ruling out the possibility of a charge-transfer complex between Ph$^{\cdot+}$ and DPE followed by its irradiation.

As a general rule, the bands appearing at the longest wavelenghts in the spectrum of a radical ion correspond to $D_o \rightarrow D_n$ transitions, in which an electron is promoted from a doubly occupied molecular orbital to the singly occupied higher molecular orbital[11, 12]. Consequently electron affinities are stronger in these excited doublet states than in the ground state. Oxidation of DPE may occur via an excited state of this type in Ph$^{\cdot+}$, but with the lack of physical data about these excited doublet states (especially their lifetime) further speculation is not possible. We are currently studying the photochemical (1), (2) and chemical (3), (4), (5) reactions of scheme II.

Acknowledgements : This research has been carried out in the laboratory of Professor G. Cauquis. We thank him for his interestand support throughout this work.

Notes and references

[1] A.J. Bard, A. Ledwith and H.J. Shine, Adv. in Phys. Org. Chem., Academic Press, London, **13**, p. 155-278 (1976).

[2] U. Svanholm and V.D. Parker, J. Amer. Chem. Soc., **94**, 5507 (1972).

[3] H. Lund and H.S. Carlsson, Acta Chem. Scand., **32**, 505 (1978), report a photochemical property of the thianthrene cation radical. The irradiation of the electrode during a cyclic voltammetry experiment on thianthrene produced an increase in the anodic peak height and a diminishing of the cathodic peak on the reverse scan.

[4] J.-P. Billon, Bull. Soc. Chim. Fr., 1784 (1960).

[5] Y. Iida, Bull. Chem. Soc. Japan, **44**, 663 (1971).

[6] Experiments with excess water are not possible because water is sufficiently basic to deprotonate $Ph^{\cdot +}$.

[7] C.E. Castro, J. Amer. Chem. Soc., **83**, 3262 (1961).

[8] R.A. Neunteufel and D.R. Arnold, J. Amer. Chem. Soc., **95**, 4080 (1973).

[9] a) V.D. Parker and L. Eberson, Chem. Comm., 340 (1969).
b) L. Eberson and V.D. Parker, Acta Chem. Scand., **24**, 3553 (1970).

[10] E. Steckhan, J. Amer. Chem. Soc., **100**, 3526 (1978).

[11] P. Cársky and R. Zahradník, Accounts Chem. Res., **9**, 407 (1976).

[12] P. Cársky and R. Zahradník, Topics in Current Chem., **43**, 1 (1973).

(Received in France 16 April 1979)