AN EFFICIENT PHOTOCHEMICAL FORMATION OF PHENOXAZINE AND PHENOTHIAZINE FROM THEIR RESPECTIVE CYCLOPENTADIENYLIRON COMPLEXES

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The photochemical liberation of phenoxazine and phenothiazine from their cyclopentadienyliron complexes was studied in THF, methanol and dimethylsulfoxide. Quantum yields of decay of the complexes and the formation of free heterocycles have been determined to be about 1·0, independent of solvent, concentration and wavelength of light used. The ease of isolation of free heterocycles after photolysis show that this efficient way of heterocycle recovery is superior to the previously utilized pyrolytic sublimation.

Synthesis of new compounds and the development of efficient or cheaper methods of synthesis of known compounds has always been of interest in synthetic organic chemistry[1]. The practical applications of photochemical methods in organic synthesis are appearing more frequently in the literature[2,3]. Such methods have been recently applied both in synthesis of η^6-arene-η^5-cyclopentadienyliron complexes and in their decomplexation leading to the preparation of free arenes. (Cp)iron complexes of p-xylene[4–6] or chlorobenzene[7] have been utilized as starting materials for preparation of numerous new complexes while photochemical demetallation of appropriate (Cp)iron complexes have led to the liberation of some interesting arenes which are hardly accesible in any other way[8,9]. In this paper we show that the photochemical decomplexation of phenoxazine or phenothiazine (Cp)iron cations is superior to the reported pyrolytic sublimation of these complexes[10].

EXPERIMENTAL

Hexafluorophosphates of (η^6-phenoxazine) (η^5-Cp)iron(II) (MOC) and (η^6-phenothiazine) (η^5-Cp)iron(II) (MTC) were prepared according to published methods[10,11] and purified by recrystallization from a mixture of acetone–methylene chloride–diethyl ether. Ferrocene (Fn), phenoxazine (PhO) and phenothiazine (PhT) obtained as a result of photolysis were separated

from inorganic products by column chromatography using silica gel and petroleum ether (Fn) and methylene chloride (PhO or PhT) as eluents, respectively.

Methanol (MeOH) for fluorescence (Merck), tetrahydrofurane (THF) for fluorescence (Merck) and dimethyl sulfoxide (DMSO) for UV-VIS spectroscopy (Merck and Fluka) were dried over molecular sieves 3 Å prior to use. A high pressure mercury lamp HBO-200 (Narva) equipped with band-pass absorption and interference filters (for 366 and 436 nm) and an argon-krypton laser ILM-120 (Zeiss, Jena G.D.R.) (for 514·5 and 647 nm) were used as the light sources. The light intensity for all wavelengths used was of the order $10^{17}-10^{18}$ photons $m^{-2}\ s^{-1}$. In qualitative studies sunlight was also used. The photochemical decay of MOC and MTC coupled with formation of Fn, PhO and PhT was investigated by UV-VIS spectroscopy (M-40 Spectrophotometer, Zeiss, Jena G.D.R.) and by emission spectroscopy using a modified MPF-3 Spectrofluorimeter (Perkin–Elmer). The formation of Fn, PhO and PhT as well as their purity were followed by GC chromatography using a PYE 105 Chromatograph fitted with columns with 5% silicon oil OV-17 or OV-101 on Gaschrom Q (100 – 120 mesh). The intensity of absorbed radiation was measured using the Reinecke salt[12,13]. Samples were deoxygenated prior to experiment by bubbling oxygen-free helium. The quantum yields of substrate photolysis and product formation were obtained by extrapolation to 0% conversion; the measurements of quantum yield were carried out under the red light. The thickness of cuvette was adjusted allowing the full measurement cycle to be performed with one and the same cuvette. This faciliated the measuring process and resulted in highly reproducible results.
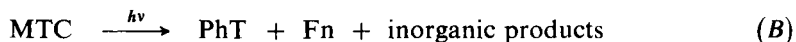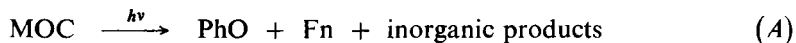
Preparation of Phenoxazine from MOC by the Photochemical Method

Deoxygenated MOC solution in MeOH (0·3 ml) of a concentration $1 \cdot 10^{-3}$ mol l^{-1} placed in a cuvette 0·1 cm thick, was irradiated at wavelength 366 nm. Source of light was a HBO-200 lamp and the light passed through an interference filter UHF 365. Phenoxazine was obtained with a 100% yield after 4 min of irradiation with the absorbed light intensity of $1\cdot5 \cdot 10^{18}$ photons $m^{-2}\ s^{-1}$. The phenoxazine was selected and purified by column chromatography and crystallization at a yield over 90%.

RESULTS AND DISCUSSION

Recently we have described synthesis of heterocycles related to anthracene with heteroatoms in the positions 9 and 10 starting from o-dichlorobenzene (Cp)iron hexafluorophosphate[10]. It involves two steps — formation of heterocycle complexed to iron (Cp) moiety and the decomplexation (liberation) of heterocycle using pyrolytic sublimation under reduced pressure. We have found that the formation of heterocycles containing sulfur and oxygen is very efficient with an overall yield of heterocycle in range 68 – 77%. For nitrogen containing heterocycles, i.e. phenoxazine and phenothiazine total yields are 22% and 5·5%, respectively. The yield of the first step involving double nucleophilic substitution cannot be improved under the conditions used[14]. The yield of the second step — liberation of heterocycle by high temperature pyrolysis under high vacuum — is very low because of thermal side reactions and may be improved. We have applied photolysis for the efficient recovery of the free heterocycles on the basis of an extensive study of the photochemistry of heterocyclic complexes.

Irradiation of MOC and MTC in the range 254 − 647 nm resulted in their photo-chemical decomposition and formation of PhO and PhT, respectively. Depending on the solvent used the formation of Fn was also observed in reactions (A) and (B) (ref.[15]).

$$MOC \xrightarrow{h\nu} PhO + Fn + inorganic\ products \qquad (A)$$

$$MTC \xrightarrow{h\nu} PhT + Fn + inorganic\ products \qquad (B)$$

Typical examples of the spectral changes observed during photolysis of deoxy-genated MOC in methanol solution are presented in Fig. 1. Four isosbestic points were observed at $\tilde{\nu}$ 28 600, 33 500, 41 000 and 44 500 cm^{-1}. Analogous spectral changes with four isosbestic points at $\tilde{\nu}$ 28 500, 32 400, 38 200 and 41 700 cm^{-1} were observed during photolysis of MTC in MeOH solution[15]. The presence of these four points in the range 0 − 100% conversion of MOC and MTC ensure an easy control of the path and mechanism of photolysis. Quantum yields of MTC decay,
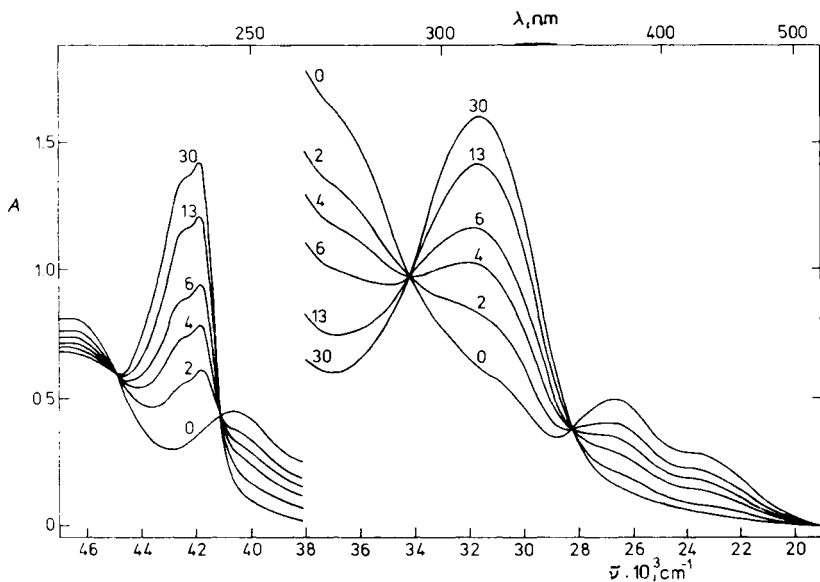

FIG. 1

Spectral changes in the UV-VIS spectra of the hexafluorophosphate of (η^6-phenoxazine) (η^5-cy-clopentadienyl) iron(II) (c 1 . 10^{-3} mol l^{-1}) in methanol under irradiation at 366 nm and 293 K. The numbers on the curves are the irradiation times in minutes. In the range 47 000 to 38 000 cm^{-1} cuvette path lengths is 0·03 cm, and in the range 38 000 − 19 000 cm^{-1} was 0·15 cm

ϕ_{MTC}, as well as quantum yield of PhT formation, ϕ_{PhT} in THF, MeOH and DMSO are given in Table I.

As shown in Table I the values of ϕ_{MTC} and ϕ_{PhT} are about 1·0 and are solvent independent. We also found that for deoxygenated MTC solution in DMSO for concentrations varying from 10^{-2} to 10^{-4} mol l^{-1} and under excitation at 514·5 and 647 nm the quantum yields ϕ_{MTC} and ϕ_{PhT} are also 1·0.

In the photochemical decay of MOC and the formation of PhO the quantum yields ϕ_{MOC} and ϕ_{PhO} are also found to be 1·0. Ferrocene, (Fn) was also found among the products of reactions (A) and (B). The quantum yield of Fn formation in both reactions is very low in MeOH and DMSO but significantly higher in THF. Because of the low values of Fn molar absorption coefficient ($\varepsilon < 100$ l mol^{-1} cm^{-1} for $\lambda \geqq 300$ nm), the contribution of Fn in the UV-VIS spectra registered during photolysis may be neglected in MeOH or DMSO for $\lambda > 290$ nm and in THF for the 300 − 360 nm range. The quantity of the Fn formed in reactions (A) and (B) was determined by a GC method and also by UV-VIS spectroscopy for reactions in THF.

As our attention was focussed on preparative aspects of the work we did not investigate the mechanism of replacement of heterocycle substituent or the formation of ferrocene. It is reasonable to assume that reactions in solvents utillized in our work might proceed in a similar way as described[16−19] even if stability of the (Cp)Fe-(solvent)$_3$ cations is even lower and they decompose to ferrocene and/or inorganic iron salts[16].

The results of our experiments show that the photochemical method of decomplexation of phenoxazine or phenothiazine (Cp)iron complexes can be succesfully used for preparative purposes. A number of advantages have emerged including: 1) selectivity of reactions (A) and (B) in a wide range of wavelength (254 − 647 nm) with the possibility of using sunlight and Pyrex equipment; 2) efficient and simple monitoring of the process using UV-VIS spectroscopy and the easy isolation of the hetero-

TABLE I

Quantum yields (ϕ_{MTC}) of MTC photolysis (c 1 . 10^{-3} mol l^{-1}) and quantum yields (ϕ_{PhT}) of PhT formation for different solvents under excitation at 366 nm

Solvent	ϕ_{MTC}	ϕ_{PhT}
THF	1·23 ± 0·25	1·22 ± 0·25
MeOH	1·04 ± 0·20	1·06 ± 0·20
DMSO	1·22 ± 0·25	1·20 ± 0·25

cycle from the solution after reaction. Finally with the quantum yields of heterocycles formation reaching value 1·0 and no following chemical changes of heterocycles in solution photochemical decomplexation of phenoxazine or phenothiazine (Cp)iron complexes is definitely superior to pyrolytic sublimation described previously.

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