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PHOTOCATALYSIS OF THE PSCHORR REACTION BY Ru(bpy)$_3^{2+}$ IN THE FLUORENONE, FLUORENE AND DIBENZOFURAN SERIES

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Summary

Photocatalysis of the Pschorr reaction by Ru(bpy)$_3^{2+}$ in the fluorenone, fluorene and dibenzofuran series occurs with a low yield and slow rate in contrast with the photocatalysis previously observed for the phenanthrene series. The addition of an irreversible electron donor (4-methoxybenzyl alcohol) accelerates the reaction significantly but does not modify the cyclized-to-uncyclized compound ratio. The latter is found to be a function of the bridging group X.

1. Introduction

We reported recently [1] the photocatalysis of the Pschorr reaction by Ru(bpy)$_3^{2+}$ (bpy, 2,2'-bipyridine) in the phenanthrene series. We have shown that the irradiation with visible light ($\lambda_{ex} > 410$ nm) of an oxygen-free acetonitrile solution of the tetrafluoroborate salt of the particular stilbene diazonium salt 1 in the presence of a catalytic amount of Ru(bpy)$_3^{2+}$ leads to the corresponding phenanthrene 2 with a high yield (100%) and a high quantum yield ($\phi > 0.4$) [1] (eqn. (1)).

$$\text{1} \xrightarrow[\text{Ru(bpy)}_3^{2+}]{h\nu} \text{2} \quad + \text{N}_2 + \text{H}^+ \tag{1}$$
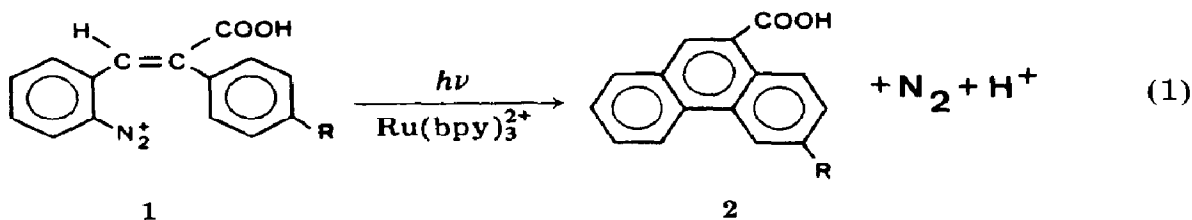
R ≡ H, Br or OCH$_3$

We report here an attempt to extend the Pschorr reaction of the diazonium salts **3**, photocatalysed by $Ru(bpy)_3^{2+}$, to the fluorenone, fluorene and dibenzofuran series.
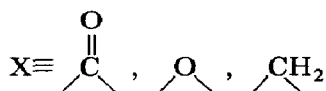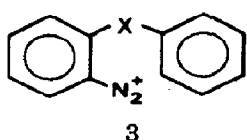
2. Experimental details

2.1. Materials

The diazonium tetrafluoroborate salts **3** were prepared following a standard procedure [2] from the corresponding 2-amino derivatives, *i.e.* 2-aminobenzophenone (Fluka), 2-aminodiphenyl oxide obtained by tin reduction [3] of 2-nitrodiphenyl oxide (Tokyo Kasei) and 2-aminodiphenylmethane (Fluka) respectively. They were purified three times by dissolving in acetonitrile followed by precipitating with anhydrous diethyl oxide and drying overnight in vacuum. They were stored under vacuum at −5 °C. Their structures were verified by fast atom bombardment mass spectroscopy. Commercial benzophenone, fluorenone, diphenylmethane, fluorene (Fluka), diphenyl oxide and dibenzofuran (Tokyo Kasei) were used without further purification for analysis by high performance liquid chromatography (HPLC). $Ru(bpy)_3^{2+}(BF_4^-)_2$ [1] and the ligand-modified complex $RuL_3^{2+}(PF_6^-)_2$ salt [4] were prepared as previously reported. Acetonitrile and tetrabutylammonium perchlorate were purified as described elsewhere [5].

2.2. Spectra and analysis

Electronic spectra were recorded on a Beckman Acta IV spectrophotometer. Luminescence quenching measurements were performed with a Jobin–Yvon JY 3C fluorescence spectrophotometer at room temperature. Stern–Volmer intensity quenching experiments were carried out using argon-degassed solutions. Six different concentrations of quenchers were used ranging from zero to that resulting in about 80% quenching. Using the Stern–Volmer relationship $I_0/I = 1 + k_q \tau_F[Q]$ where k_q is the quenching rate constant, τ_F the lifetime of the excited state ($\tau_F = 855$ ns in CH_3CN at 298 K [6] for $Ru(bpy)_3^{2+}$), plots of I_0/I against $[Q]$ permit k_q to be determined [7]. Cyclic voltammograms were obtained by using a PAR 173 potentiostat and a PAR 175 universal programmer. Potentials of the cathodic peak of **3** (E_{p_c}) were measured in CH_3CN + 0.1 M n-Bu$_4$-$NClO_4$ at a platinum electrode (sweep rate, 0.1 V s^{-1}) and are reported relative to the Ag/10 mM Ag$^+$ reference electrode. HPLC analysis was performed on Waters Radialpak silica or μ Bondapak CN columns using a Waters Associates Instruments high performance liquid chromatograph (eluted with different mixtures of heptane–CH_2Cl_2) equipped with a printer–

plotter—integrator Waters Associates data module. Assays were made using an external standard.

2.3. Photolysis system

The photolysis apparatus for preparative experiments consists of an Osram 250 W xenon lamp equipped with T_2 and Ta_2 IR filters ($\lambda < 800$ nm) obtained from Metallisation Traitement Optique and a 3.73 ($\lambda > 410$ nm) Corning filter to select the desired area of the visible spectrum [8]. Throughout the irradiation, the sample solution was thermostatted at 0 ± 2 °C by an ethanol stream through a glass jacket to prevent the slow thermal decomposition of 3.

3. Results and discussion

The salts 3 quench the luminescence of the excited state $Ru(bpy)_3^{2+*}$ in deaerated acetonitrile as in the same way for the regular para-substituted benzene diazonium salts [9]. The quenching process is a simple bimolecular reaction since the Stern—Volmer plots are linear. The quenching rate constants k_q are found to be diffusion controlled ($k_q = 2.5 \times 10^{10}$ M^{-1} s^{-1} ($X \equiv {>}C{=}O$), 2.3×10^{10} M^{-1} s^{-1} ($X \equiv -O-$), 1.3×10^{10} M^{-1} s^{-1} ($X \equiv -CH_2-$)) in agreement with the easy reduction of 3 ($E_{p_c}(V) = -0.25$ ($X \equiv {>}C{=}O$), -0.31 ($X \equiv -O-$), -0.45 ($X \equiv -CH_2-$)) if it is assumed that quenching operates by electron transfer.

Proof of the electron transfer mechanism is obtained by continuous photolysis of the $Ru(bpy)_3^{2+}$–3 system.

Selective irradiation ($\lambda_{ex} > 410$ nm) of 2×10^{-4} M $Ru(bpy)_3^{2+}$ and 5×10^{-3} M 3 ($X \equiv {>}C{=}O$) in argon-purged acetonitrile induces the rapid photogeneration of the $Ru(bpy)_3^{3+}$ species. A similar phenomenon was observed by using a ligand-modified ruthenium complex designated RuL_3^{2+}
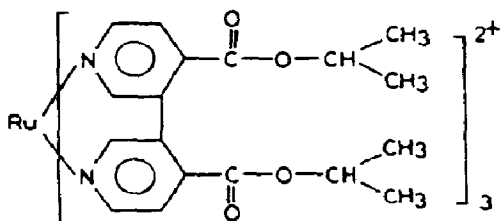
which is 0.3 V less easily oxidized [4] than $Ru(bpy)_3^{2+}$. For instance, spectral changes during irradiation illustrate RuL_3^{3+} photogeneration (see Fig. 1). The last spectrum is identical with the authentic spectrum of RuL_3^{3+} [4]. However, several hours of photolysis of the solution induces a slow consumption of 3. Quantitative HPLC analysis during the irradiation indicates the formation of benzophenone and fluorenone. Data related to this transformation are reported in Table 1.
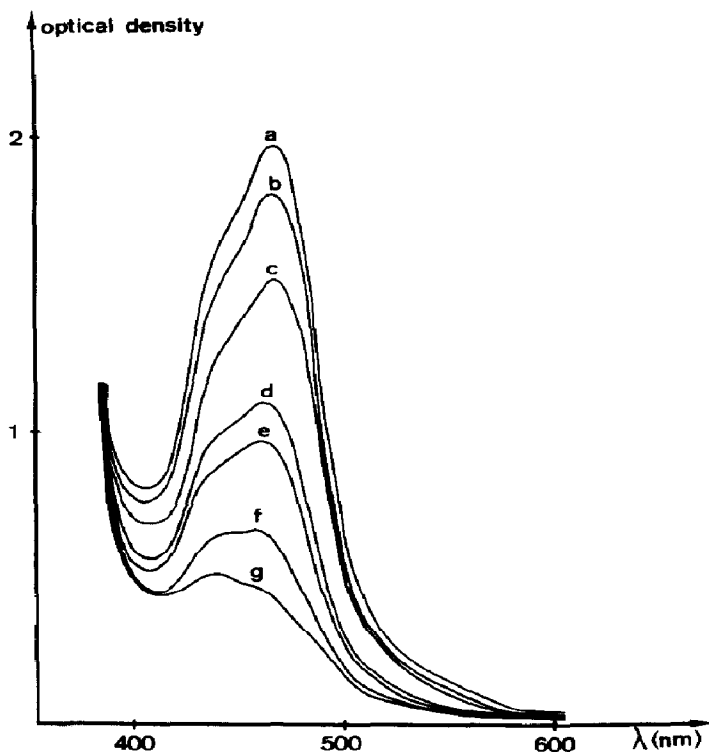
Fig. 1. Spectral change during irradiation at $\lambda_{ex} > 410$ nm of $RuL_3^{2+}(1.3 \times 10^{-4}$ M) with **3** ($X \equiv \,>C=O$) (5×10^{-3} M) in CH_3CN: curve a, $t = 0$ s; curve b, $t = 10$ s; curve c, $t = 36$ s; curve d, $t = 1$ min 11 s; curve e, $t = 2$ min; curve f, $t = 3$ min 30 s; curve g, $t = 6$ min 45 s.

TABLE 1

Photodecomposition of **3** ($X \equiv \,>C=O$) in the presence of $Ru(bpy)_3^{2+}$

| Time of irradiation (h)	Amount of 2 consumed (%)	Fluorenone-to benzophenone ratio
1	4.3	0.52
5	21	0.56
22	63	0.22

In contrast with the observation [1] with the diazonium compounds **1**, it appears from these results that cyclization of the free aryl radical **4** (eqn. (2))


$$(2)$$
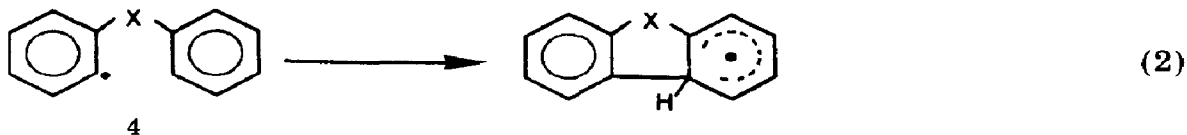
formed from the electron transfer quenching of $Ru(bpy)_3^{2+*}$ by 3 ($X \equiv$ $\searrow C=O$) (eqns. (3) - (5))

$$Ru(bpy)_3^{2+} \xrightarrow{h\nu} Ru(bpy)_3^{2+*} \qquad (3)$$


$$(4)$$

$$(5)$$
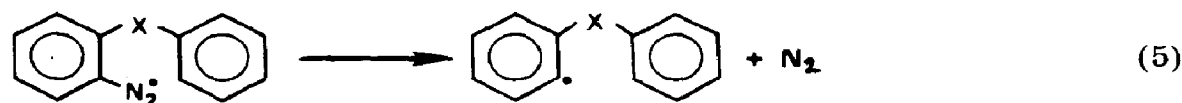
is largely prevented by its change into the corresponding uncyclized hydro-carbon (benzophenone). The latter probably results from hydrogen abstraction from acetonitrile (eqn. (6)), as reported for benzene diazonium salts [9] acting as electron-transfer quenchers of $Ru(bpy)_3^{2+*}$.

$$(6)$$
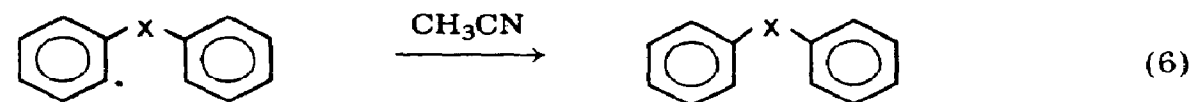
The cyclization of the free aryl radical 4 is markedly less efficient than that of the corresponding radical resulting from the electron transfer between $Ru(bpy)_3^{2+*}$ and 1. This difference has its origin in the structure of this free radical since rigidity of the molecule 1 and aromaticity of the resulting molecule 2 are in favour of its cyclization [10]. The slowness of the photocatalysis results from the poor yield of regeneration of $Ru(bpy)_3^{2+}$ (eqn. (7)) because of the reduction of the photogenerated $Ru(bpy)_3^{3+}$ by the cyclized form of the radical 4. This key transitory species leads to the cation 5 which gives fluorenone by loss of a proton (eqn. (8)).

$$(7)$$

5

$$(8)$$
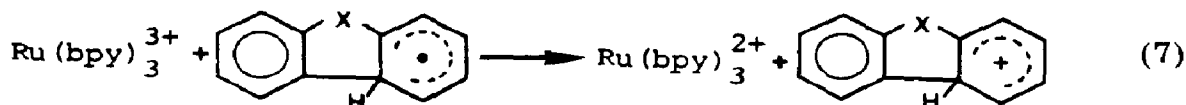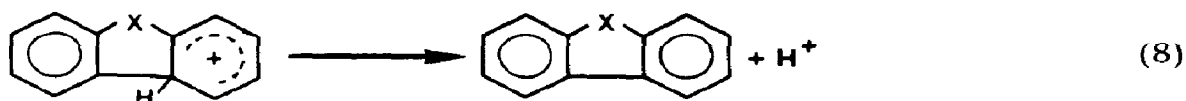
For the other diazonium salts ($X \equiv -O-$ and $-CH_2-$) consumption of 3 by visible photolysis in the presence of $Ru(bpy)_3^{2+}$ is slower than for the case where $X \equiv \searrow C=O$ since, for example, only 20% of 3 ($X \equiv -O-$) disappears after 24 h. These results indicate clearly that, for diazonium salts 3, photocatalysis of the Pschorr reaction by $Ru(bpy)_3^{2+}$ occurs with a low yield and with a slow rate.

In order to accelerate the $Ru(bpy)_3^{2+}$ regeneration, an irreversible electron donor, easily oxidized by $Ru(bpy)_3^{3+}$, is added to the system $Ru(bpy)_3^{2+}-3$. We have previously shown that carbinols such as 4-methoxybenzyl alcohol are easily photo-oxidized in basic media to their corresponding aldehydes by the $Ru(bpy)_3^{2+}$–diazonium system [11]. Consequently, we have studied the photolysis of the $Ru(bpy)_3^{2+}-3$ system (2×10^{-4} M and 1.0×10^{-2} M respectively) in the presence of a half-stoichiometric amount of 4-methoxybenzyl alcohol with collidine (1.5×10^{-2} M) as a basic agent. Complete disappearance of 3 is achieved after about 0.5 h and Table 2 gives the percentage of the corresponding cyclized and uncyclized compounds. Thus, addition of 4-methoxybenzyl alcohol significantly accelerates the photocatalysis rate. However, no major modification of the product distribution is observed since, for instance, with $X \equiv {>}C{=}O$, 25% of fluorenone is obtained as compared with 18% in the absence of added electron donor.

The following scheme summarizes the mechanism involved.

4. Conclusion

It appears that the efficiency of the Pschorr reaction in acetonitrile is strongly dependent on the bridging group X. The percentage of the
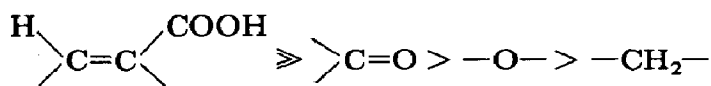
TABLE 2

Photodecomposition of 3 in the presence of $Ru(bpy)_3^{2+}$ and 4-methoxybenzyl alcohol

X	Yield [a] of cyclized compounds (%)	Yield [a] of uncyclized compounds (%)
$>C=O$	25	75
$-O-$	10	90
$-CH_2-$	0	100

[a] Ratio of product formed to 3 consumed.

cyclized compound decreases in the order

$$\underset{H}{\overset{}{>}}C=C\overset{COOH}{\underset{}{<}} \gg \ >C=O > -O- > -CH_2-$$

This order is in good agreement with that observed for the copper-catalysed Pschorr reaction in which an electron-transfer mechanism has also been propounded [12]. As an extension of this work, it would be interesting to test this $Ru(bpy)_3^{2+}$ photocatalysis in a worse hydrogen-donating solvent than acetonitrile in order to increase the yield of the cyclization product.

Acknowledgments

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