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PHOTOCHEMICAL SUBSTITUTION OF HALOARYL KETONES BY PHENYLTHIOLATE ANION

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Summary

The reactions between 4-bromobenzophenone, 4-haloacetophenones and phenylthiolate in acetonitrile, dimethyl sulphoxide and dimethyl formamide were quantitatively studied under photostimulation. Results complementing those obtained by electrochemical methods were obtained. Besides the substitution product the reduction product (3%) and diphenyl disulphide (10% - 20%) are formed. The $S_{RN}1$ mechanism of this reaction was confirmed by an overall quantum yield of greater than unity and through quenching studies using 1,4-benzoquinone or tetracyanoquinodimethane. The initial overall quantum yield was related linearly to $I^{-1/2}$ and to the nucleophile concentration, suggesting quadratic termination steps. Competitive experiments between 4-haloacetophenones confirmed the previously reported order of reactivity Br > Cl > F. From a synthetic point of view, the electrochemical process has a slight advantage because of byproduct recycling.

1. Introduction

One of the main general features arising from the last decade of studies in photochemistry is the remarkable overlap of this topic with electrochemistry [1, 2]. Several electrochemically induced chemical transformations now have their photochemical counterparts [3]. Unfortunately, even if the loose correspondence [2] between some of the photochemical and the electrochemical results is widely recognized, there are only a few studies [4] whose goal is a quantitative comparison of results obtained photochemically and electrochemically under similar experimental conditions (of substrate, temperature, concentration and solvent). The goal of the present work is just such a comparison. The reaction of phenylthiolate (PhS⁻) with 4-bromobenzophenone has been quantitatively studied by Saveant and coworkers [5, 6].

In this paper we report and discuss the quantitative results obtained for this reaction when it is photochemically induced under experimental conditions close to those selected in the electrochemical studies [5].

2. Results and discussion

2.1. General aspects

4-bromobenzophenone, 4-bromoacetophenone and its fluoro and chloro analogues react in CH_3CN, dimethyl sulphoxide (DMSO) or dimethylformamide (DMF) (all poor hydrogen donors) with the PhS^- anion under thermal (60 °C) or photochemical ($\lambda > 330$ nm) activation. Besides the substitution products, benzophenone or acetophenone are formed (through reduction of the C—X moiety) together with diphenyl disulphide (PhSSPh) (coupling of the phenylthiyl radicals). The yield and the rate of haloderivative consumption depend on the irradiation time, the light intensity and the nucleophile concentration. The results are summarized in Table 1.

$$PhS^{\cdot} + PhS^{\cdot} \longrightarrow PhS\text{-}SPh$$

$$X = F, Cl, Br$$
$$R = Me, Ph$$
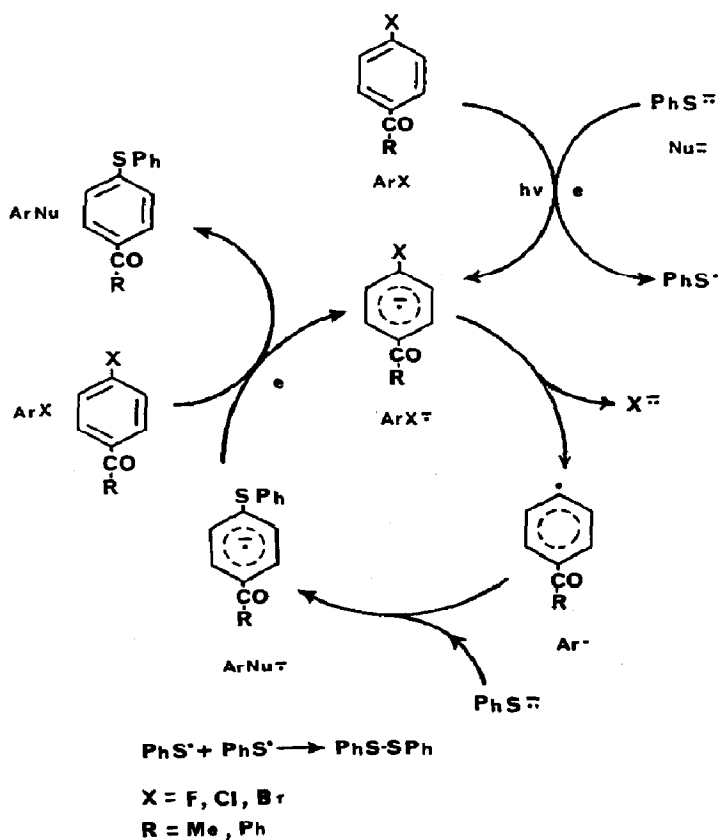
For the photochemical substitution, the incident light was filtered with a freshly prepared 2.5×10^{-2} M aqueous solution of PhS^- so that the nucleophile was not excited and the phenyl thioaryl ketone was not photolysed. In

TABLE 1

Photosubstitution of 4-bromobenzophenone and the 4-haloacetophenones 4-XC_6H_4COR by phenylthiolate PhS^-M^+: summary of quantitative results

R	X	Solvent	Nu	[Nu]/[ArX]	ArX unreacted (%)	ArNu (%)	ArH (%)	Reaction time (h)	Thermal (Δ) or hν
C_6H_5	Br	DMF	$PhS^-Bu_4N^+$	2	13.5	83	3	1.5	hν
—	—	—	—	2	9	88	3	0.5	Δ
—	—	—	PhS^-Na^+	2	0	98	2	0.5	Δ
—	—	DMSO	—	2	19	95.5	4.5	1	hν
—	—	—	—	5	1	97	3	3	hν
—	—	CH_3CN	PhS^-K^+	5	10	86.5	3.5	1	hν
—	—	—	$PhS^-Bu_4N^+$	5	58	39	3	0.5	hν
CH_3	—	DMF	PhS^-Na^+	5	0	97	3	1	Δ
—	—	—	PhS^-Na^+	5	0	96.5	3.5	7	hν
—	—	DMSO	$PhS^-Bu_4N^+$	5	23	74	3	5	hν
—	—	CH_3CN	PhS^-K^+	2	25	72	3	4	hν
—	Cl	DMF	PhS^-Na^+	5	13	84	3	20	Δ
—	—	—	PhS^-Na^+	5	10	87	3	4	hν
—	—	DMSO	$PhS^-Bu_4N^+$	5	23	74.5	2.5	12	hν
—	F	DMF	PhS^-Na^+	5	5	92	3	30	hν
—	—	—	PhS^-Na^+	5	10	87	3	6	Δ
—	—	DMSO	$PhS^-Bu_4N^+$	5	22	76	2	18	hν

PhSSPh was not accounted for in the mass balance calculation.

consequence, the PhSSPh formed did not undergo photofragmentation and thus it accumulated in the medium. So the photochemical activation ($\lambda >$ 330 nm) excited only haloaryl ketones (PhS$^{\ddot{-}}$ absorbs at 300 nm) and induced an electron transfer between the phenylthiolate Nu$^{\ddot{-}}$ (donor) and the ketone ArX (acceptor). We also found that the irradiation in less polar solvents under otherwise identical reaction conditions, or without the presence of nucleophile, induced a far slower homolysis of the C—X bond of 4-bromobenzophenone (10% conversion after 50 h). Thus, the ArX^{-} radical anion is, we believe, the initiator in the electron transfer catalysis cycle, as previously proposed by several researchers [6, 7, 17] for this system.

In CH$_3$CN, we identified the byproducts 1-cyano-2-phenylethane (less than 0.5%) and tributylamine (less than 0.5%) if the tetrabutylammonium cation is the counter-ion of the PhS^{-} anion.

In contrast to the electrochemical substitutions [6, 7] we did not observe any enhancement of the photochemical reactivity when using tetrabutylammonium phenylthiolate instead of the sodium or potassium salt. However, PhSSPh was formed (yield, 10% - 20%) in each photochemical experiment, in contrast to the reaction triggered with a cathode tuned to −1.8 V [6]. Any PhSSPh that forms in the electrochemical experiment cannot accumulate in the medium; its reduction potential is −1.8 V(SCE) (SCE, standard calomel electrode) [8] and it is reduced at the cathode, thereby regenerating the original nucleophile:

$$Ph—S—S—Ph \xrightarrow{e^-} Ph—S—S—Ph^{\dot{-}} \longrightarrow PhS^{\ddot{-}} + PhS\cdot$$
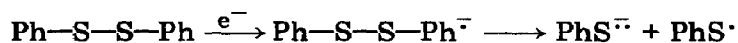
In addition, the intermediate PhS$^{\cdot}$ may also possibly be reduced to PhS$^{\ddot{-}}$ at the electrode.

2.2. Quantum yield

The S$_{RN}$1 mechanism for this reaction is confirmed in the case of photochemical activation because the observed quantum yield values are greater than unity, as reported in Table 2, and because the reaction occurs only in polar solvents such as DMF, DMSO or CH$_3$CN.

For the electrochemical substitution, the number of faradays passed through the electrolytic cell per mole of starting material (faradaic yield) was 0.2 [5]. This should correspond to 0.2 photons mol^{-1} ($\Phi = 5$) for the photo-catalysed process. This quantum yield depends on the nucleophile concentration (Section 2.5). For the same ratio [Nu]/[Ar] = 10 we measured $\Phi = 6.2$ for the initial rate of the reaction. Nevertheless, on a preparative scale, our own photochemical results suggest that the overall quantum yield for a high conversion process is less than 5.

2.3. Effect of redox inhibitors

The use of redox inhibitors as diagnostics for the S$_{RN}$1 mechanism has been described previously [9]. The results in Table 3 quantitatively illustrate this effect.

TABLE 2

Quantum yield Φ_{dis} for the reaction of disappearance of the substrate (360 nm)

Substrate ArX	[Nu]/[ArX]	Irradiation time (min)	Φ_{dis}
4-Bromobenzophenone	2.5	3	3.5
—	2.5	5	3.36
—	10	1	6.2
4-Bromoacetophenone	3	3	2.9
—	6	3	3.9

Substrate concentration, 10^{-2} M; nucleophile, $PhS^{-}Bu_4N^{+}$; solvent, DMSO.

TABLE 3

Quenching of the photochemical reaction by tetracyanoquinodimethane and 1,4-benzoquinone

$\dfrac{[\text{Quencher}]}{[\text{ArX}]} \times 10^3$	Tetracyanoquinodimethane		1,4-Benzoquinone	
	ArX consumed (%)	Φ_{dis}	ArX consumed (%)	Φ_{dis}
0	47.7	3.5	46.2	3.5
0.25	37.5	2.7	40.1	3.0
0.5	36.0	2.6	37.3	2.8
0.75	34.8	2.5	31.9	2.4
1.25	27.3	2.0	22.6	1.7
1.875	22.7	1.66	18.2	1.4
2.5	21.8	1.59	13.0	1.0
3.125	15.1	1.10	10.5	0.8
4.375	12.3	0.9	5.3	0.4

Substrate, 4-bromobenzophenone (10^{-2} M); nucleophile, $PhS^{-}Bu_4N^{+}$ (5×10^{-2} M); solvent, DMSO; irradiation time, 7 min.

1,4-Benzoquinone (BQ) and tetracyanoquinodimethane (TCNQ) both reduce the reaction rate (and Φ) of the photochemical reaction even at low concentrations (about 0.25 mol.%). The same holds true for the thermal reaction. BQ displays the greater inhibitory effect. This does not agree with the known redox potentials: $E_{1/2} = -0.40$ V(SCE) for BQ [10] and 0.18 V(SCE) for TCNQ [11]. TCNQ should be the better electron acceptor.

We assume that the inhibition displayed is due to the quenching of the radical vectors of the $S_{RN}1$ chain reaction. Indeed, the inhibitory effect operates at very low concentrations of inhibitor: the [quencher]/[substrate] ratios are of the order of 10^{-3}. It is unlikely that the effect originates from the removal of the corresponding concentration of free nucleophile by electron donor–acceptor interactions.

The reaction rate also decreases when small amounts of 1,4-dinitrobenzene (1 mol.%) are added. However, this effect may result from electron-transfer quenching or through competition with bromobenzophenone for

the absorption of light (internal-filter effect). The results do not distinguish between these two effects. Note that 1,4-dinitrobenzene strongly absorbs incident light in the region 340 - 360 nm which is the same region in which the n → π* transition of the haloaryl ketones studied is observed.

2.4. Overall quantum yield variation with irradiation time

The overall quantum yield for the disappearance of 4-bromobenzophenone decreases with the time of irradiation of the substrate (Table 4). A negative side of this effect is that it is difficult to consume completely the substrate (e.g. in Table 1, note the irradiation time necessary to obtain 80% conversion of the original haloaryl ketones). This self-inhibition of the reaction is unlikely to be due to energy transfer quenching by one of the reaction products (ArNu or ArH), since 4-bromobenzophenone does not photosensitize the decomposition of benzophenone or 4-phenylthiobenzophenone. Thus substitution-product yields of 95% were obtained for an irradiation time of 1.5 h.

Another explanation may be the lowering of the rates of the second-order chain-carrying steps versus the (probably) first-order termination steps. This agrees with the kinetic behaviour observed for the thermal reaction being similar to that for the photochemical reaction.

To minimize quantitative problems connected with self-inhibition, the determinations of the variations in the quantum yield with the reaction parameters and with the inhibitory effects of the electron acceptors were performed at low conversions (5% - 15%).

TABLE 4

Rate of the disappearance of the substrate with irradiation time

Irradiation time (min)	Disappearance of the substrate (%)	Φ_{dis} (overall)
3	23.4	3.5
5	36.8	3.36
7.5	43.7	2.66
10	48.4	2.21
15	50.9	1.55
20	55.2	1.26

Substrate, 4-bromobenzophenone (10^{-2} M); nucleophile, $PhS^-Bu_4N^+$; [Nu]/[ArX] = 2.5; solvent, DMSO; Pyrex filter plus 1 cm aqueous solution PhS^-K^+; Hanau Q.81 lamp; intensity, 1.75×10^{-4} einsteins l^{-1} min^{-1}.

2.5. Variation in quantum yield with intensity of irradiation and concentration of nucleophile

The $S_{RN}1$ mechanism often corresponds to a chain reaction initiated by a photoinduced electron transfer. The dependence of the overall quantum yield on reactant concentration and absorbed light intensity has been treated

kinetically by several researchers. In the absence of a charge transfer complex between the donor and the acceptor, as in our case, and if all the incident light is absorbed by the substrate, Stranks and Yandell [12] and Tolbert [13] propose that the overall quantum yield is proportional to the nucleophile concentration Nu^- and to $I^{-1/2}$. The variation in Φ with these parameters provides further information on the nature of the termination steps [14, 15].

The results displayed in Fig. 1 show that for 4-bromobenzophenone Φ varies linearly with $I^{-1/2}$. Such a variation implies quadratic termination steps, as was noted by Stranks and Yandell. Adamson and Sporer observed the same behaviour for the photoinduced chain exchange of $PtBr_6^{2-}$ with Br^- [16].

The variation we observed suggested termination steps involving two radicals or radical anions:

$$Ar^{\cdot} + Ar^{\cdot} \longrightarrow Ar\text{—}Ar \tag{1}$$

$$Ar^{\cdot} + ArX^{\cdot -} \longrightarrow Ar^{\cdot -} + ArX \tag{2}$$

$$Ar^{\cdot} + ArNu^{\cdot -} \longrightarrow Ar^{\cdot -} + ArNu \tag{3}$$

This is possibly followed by

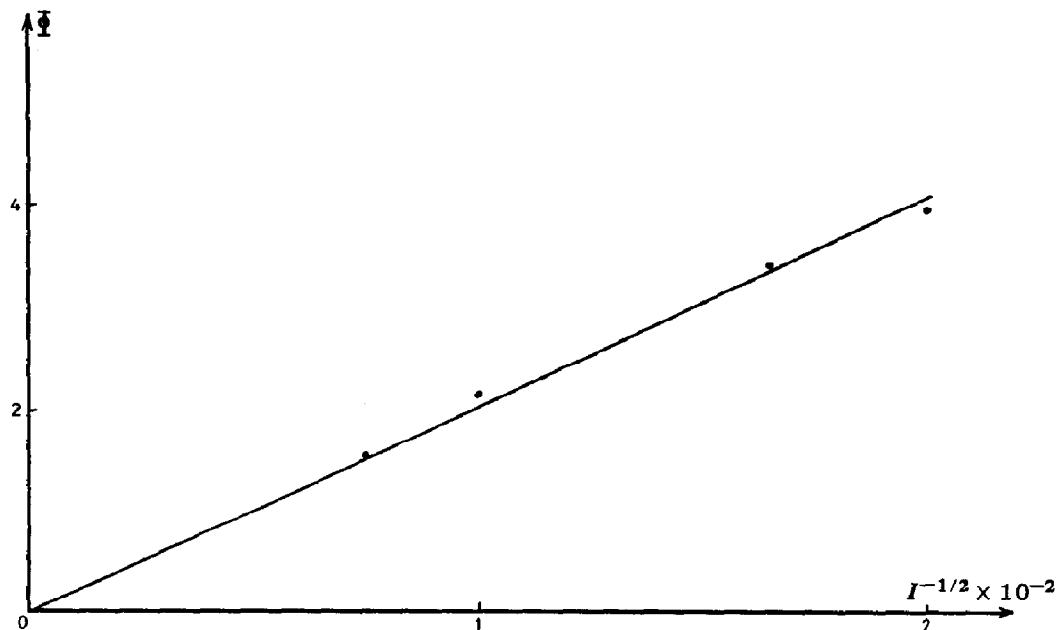$$Ar^{\cdot -} + SH \longrightarrow ArH + S^{\cdot -} \tag{4}$$

Fig. 1. Variation in the disappearance quantum yield with the incident light intensity. Substrate, 4-bromobenzophenone (10^{-2} M); nucleophile, $PhS^-Bu_4N^+$ (2×10^{-2} M); solvent, DMSO; the intensity is in einsteins per litre per minute.

(SH, solvent). $Ar^{\cdot -}$ is unlikely to result from electron transfer between $Ar^{\cdot} + Nu^{\cdot -}$, *i.e.*

$$Ar^{\cdot} + Nu^{\cdot -} \longrightarrow Ar^{\cdot -} + Nu^{\cdot} \tag{5}$$

since we found that the ArH yield did not increase when the nucleophile concentration was increased. We observed the reduction products ArH (benzophenone or acetophenone) in every experiment. We therefore propose that, even for photochemical stimulation, the termination steps involved are the same as those reported by Saveant and coworkers [5] from electrochemical studies: (2) or (3) followed by (4). Thus, at this level, there is apparently nothing to differentiate between the termination steps involved in the electrochemical experiments and the photochemical experiments (but note the difference concerning PhSSPh formation, Section 2.1).

Figure 2 shows that for a constant concentration of 4-bromobenzophenone the value of the overall quantum yield is approximately linear
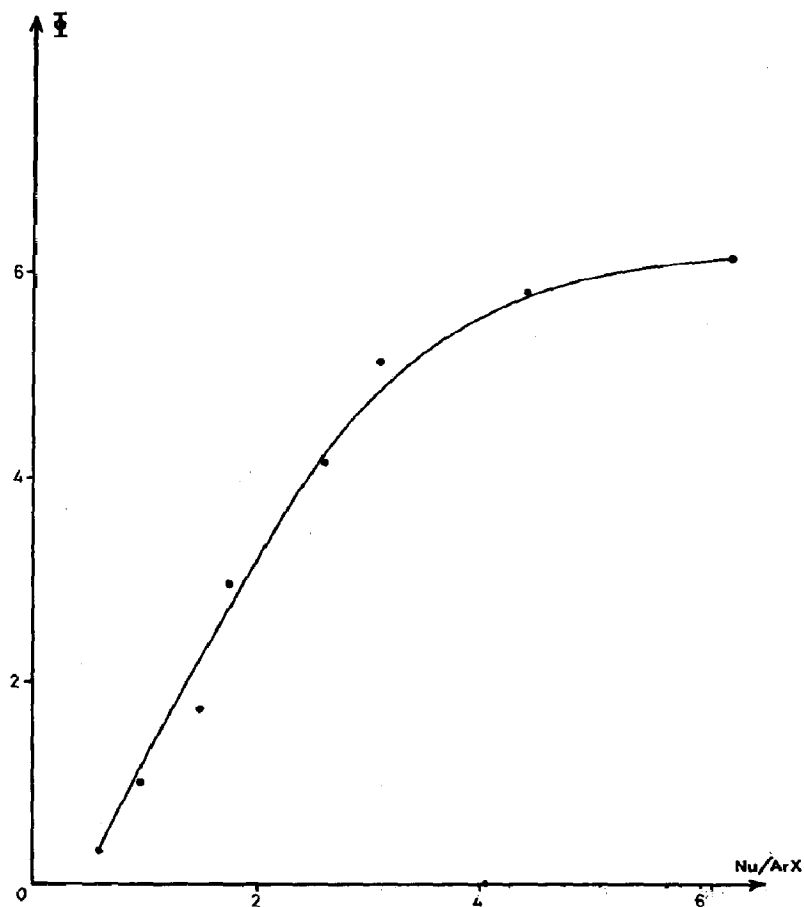

Fig. 2. Variations in the quantum yield with the nucleophile concentration. Substrate, 4-bromobenzophenone (10^{-2} M); nucleophile, $PhS^- Bu_4N^+$; irradiation time, 3 min; solvent, DMSO.

with nucleophile concentration until a limiting value of $[Nu]/[Arx] = 3$ is reached.

Tolbert [13] has proposed a limiting expression of the quantum yield for a chain process involving a linear relationship with nucleophile concentration. Stranks and Yandell [12], for the photoinduced electron exchange chain reaction between Tl^{III} and Tl^{I}, showed that the observed overall quantum yield was directly proportional to the concentration of each of the reactants. They also observed that, for higher concentrations, the quantum yields reached a plateau, in agreement with our experiments.

The analysis of Hoz and Bunnett [17] of the photosubstitution of iodobenzene by potassium diethylphosphite was complicated by the existence of a charge transfer complex (CTC) between the reactants. Dividing the raw quantum yield by the fraction of light absorbed by the substrate, these researchers obtained a corrected value of Φ corresponding to the situation where the photons absorbed by iodobenzene are also the photons which stimulate the reaction. This corrected quantum yield was found to be linearly related to the nucleophile concentration. This result agrees with our results for the linear portion of the plot of Φ versus $[Nu]/[ArX]$. Because of the CTC, these researchers were unable to conclude whether it was the absorption of photons by the CTC or by the substrate which was responsible for the stimulation of the reaction. Therefore, they proposed that the rate law obtained resulted from a combination of the two phenomena.

We found the same results as Bunnett. Since no CTC is involved, the reaction is first order in nucleophile and zeroth order in substrate concentration.

2.6. Competitive reactions between the haloacetophenones

Under irradiation, competitive experiments between 4-fluoroacetophenone, 4-chloroacetophenone and 4-bromoacetophenone confirmed the previously reported order of reactivity $Br > Cl > F$ corresponding to a long-chain situation (see Table 5). In such a case, the propagation step plays the major role and the results of both Saveant and coworkers [18, 19] and Behar and Neta [20], although quantitatively different, agree with this order of reactivity for the dehalogenation rate of the same radical anions.

3. Conclusions

This study of an electron-transfer-induced chain reaction through electrochemical [5 - 7] and photochemical methods illustrates the similarities and differences between the two techniques.

The similarities are the same approximate yield (with a slight advantage to the electrochemical study), the same primary termination step, the same initiation step (in previous studies, it was not possible to draw this conclusion because of the formation of a CTC) and the comparable chain length involved.

TABLE 5

Competitive experiments between 4-haloacetophenones

X	Solvent	Irradiation time (h)	ArX consumed (%)
F	DMF	4	14
Cl	—	4	33
Br	—	4	68
F	CH$_3$CN	2	3
Cl	—	2	19
Br	—	2	60
F	DMF	1	2
Cl	—	1	17
Br	—	1	51

[4-XC$_6$H$_4$COCH$_3$] = 10^{-2} M; nucleophile, PhS$^-$Bu$_4$N$^+$; [Nu]/[ArX] = 5.

The main difference is the production of small amounts of diaryl disulphide in the photochemical experiment together with about 3% of the reduction product. From a synthetic point a view this gives a definite advantage to the electrode process (i.e. recycling of byproducts) for this reaction.

Although for this specific case, electrochemistry is better suited from a preparative point of view, more examples are necessary to decide if this conclusion is generally correct.

4. Experimental details

4.1. General methods

The UV spectra were recorded using a Beckman M 25 spectrometer. Gas chromatography (GC) analyses were performed using an Intersmat IGC 15 fitted with a flame ionization detector. A 2 m × 1/8 in stainless steel column packed with 10% silicone SE 30 on Chromosorb WAW DMCS (80 - 100 mesh) was used with helium as the carrier gas. The chromatograph was coupled to a Spectra Physics Minigrator integrator.

The mass spectra were obtained by gas chromatography–mass spectroscopy (GC–MS) using a Ribermag 10-10 instrument fitted with a silica capillary column (CP Sil 5, 25 m × 0.32 mm). The carrier gas was helium.

4.2. Materials

CH$_3$CN, DMSO and DMF were dried over 4 Å molecular sieves, distilled and stored over molecular sieves.

The starting compounds were of commercial origin (Fluka, purum) and were used without further purification. PhSSPh was obtained commercially (Fluka). 4-Phenylthiobenzophenone was prepared by the Friedel–Crafts reaction between PhSSPh and benzoyl chloride according to ref. 21. 4-Phenylthioacetophenone was obtained by preparative GC from the reaction mixture.

4.3. Synthesis of the nucleophiles

Tetrabutylammonium phenylthiolate was prepared by mixing stoichiometric amounts of the thiol with a 40 vol.% aqueous solution of tetrabutylammonium hydroxide in the solvent to be used (DMSO, DMF etc.) and drying the resulting solution over 4 Å molecular sieves.

Sodium and potassium phenylthiolates were prepared by mixing stoichiometric amounts of the thiol with sodium or potassium hydroxide in methanol and drying the resulting solutions over 4 Å molecular sieves. The solvent was then removed by evaporation and the residual PhS$^-$ stored under vacuum. (These thiolates are slowly oxidized to the corresponding diphenyl disulphide in air.)

4.4. Identification of the products

The products of the reaction were identified by comparison with authentic samples in GC analyses and by GC–MS analysis. The following mass spectra were indicative of the products.

4-Phenylthioacetophenone ($C_{14}H_{12}OS$): 229, 228 (0.15, 0.74) M$^+$; 214, 213 (0.16, 1) [M—CH$_3$]$^+$; 185, 184 (0.08, 0.4).

4-Phenylthiobenzophenone ($C_{19}H_{14}OS$): 291, 290 (0.21, 1) M$^+$; 214, 213 (0.12, 0.87) [M—C$_6$H$_5$]$^+$; 185, 184 (0.08, 0.5).

Acetophenone (C_8H_8O): 120 (0.55) M$^+$; 105 (1) C$_6$H$_5$CO$^+$; 77 (0.78) C$_6$H$_5^+$.

Benzophenone ($C_{13}H_{10}O$): 182 (0.33) M$^+$; 105 (1) C$_6$H$_5$CO$^+$; 77 (0.67) C$_6$H$_5^+$.

PhSSPh ($C_{12}H_{10}S_2$): 220, 219, 218 (0.10, 0.16, 1) M$^+$; 110, 109 (0.25, 0.79) C$_6$H$_5$S$^+$.

4.5. Thermal activation

Thermal reactions were conducted with the same solvents and concentrations as in the photochemical procedures but in a water bath thermostatted at 60 °C.

4.6. Photochemical techniques

The photochemical reactions were performed in a "merry-go-round" apparatus fitted with 20 5 ml tubes.

The lamp used was a medium pressure mercury lamp (HANAU Q 81) cooled by a Pyrex water jacket. The radiation was filtered by a second cylindrical vessel (optical path, 1 cm) containing a freshly prepared 2.5 × 10^{-2} M aqueous solution of PhS$^-$.

The results for different intensities were obtained by placing cylindrical grids of different porosities around the equipment described above.

Quantitative experiments and competitive reactions were performed by using the merry-go-round apparatus with different concentrations of nucleophile, or redox inhibitors, in different tubes. The irradiation time was the same for all the tubes, and the disappearance of the substrate was monitored

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by gas–liquid chromatography analysis with hexadecane (for haloaceto-phenones) or docosane (for bromobenzophenone) as the standard.

4.7. Quantum yield measurements

The quantum yield measurements were performed in a merrry-go-round apparatus by using potassium ferrioxalate as the chemical actinometer. The 340 nm wavelength was selected by an especially constructed grating monochromator with a bandwidth of 20 nm. The light source was a high pressure mercury lamp (OSRAM HBO 1000 W).

The actinometer tubes were randomly irradiated ten times, each for a duration of 1 min. The ferrioxalate concentration was adjusted to 10^{-2} M so that its optical density was greater than 2 after irradiation.

The rate of disappearance of the substrate was determined by GC analysis with docosane as the standard. Since the transformation rate (percent disappearance of starting material) was small (2% - 5%) the absorption band of the substrates at 340 nm remained well resolved and unmasked.

4.8. Photochemical reaction of phenylthiolate with 4-bromobenzophenone

To 4 ml of a 10^{-2} M solution of 4-bromobenzophenone (in CH_3CN, DMF or DMSO) were added 80 μl ([Nu]/[ArX] = 2) to 200 μl ([Nu]/[ArX] = 5) of a 1 M solution of PhS^- in the same solvent.

The tube was deaerated for 15 min with a flow of nitrogen, closed with a glass stopper and then irradiated until the desired conversion of the substrate was obtained.

The excess nucleophile was then destroyed by adding one drop of commercial acetic acid, and 200 μl of a 0.1 N solution of docosane (internal standard) was added. The resulting mixture was analysed by GC, as described previously.

4.9. Photochemical reaction of phenylthiolate with 4-haloacetophenones

The procedure was the same as that described above, but the internal standard used was hexadecane.

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