Distinct fragmentation patterns of the radical anions derived from 1-halo-2- and -4-(phenylmethylthio)benzenes

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Received (in Cambridge, UK) 26th October 1999, Accepted 24th December 1999

Irradiation of 1-bromo-2-[(phenylmethyl)thio]benzene (**1**), 1-iodo-2-[(phenylmethyl)thio]benzene (**2**), and 1-iodo-4-[(phenylmethyl)thio]benzene (**3**), in DMSO as solvent in the presence of pinacolone enolate ion led to entirely different product distributions. Thus, irradiation of **1** afforded exclusively fragmentation of the C–S bond of the thiobenzyl moiety, yielding bibenzyl and 2-bromobenzenethiol, whereas irradiation of **2**, under the same reaction conditions, afforded the intramolecularly-cyclized product benzothiochromene (**9**), which arises from a C–I bond scission.

Irradiation of **3**, in DMSO as solvent and in the presence of pinacolone enolate ion, afforded *p*-iodobenzenethiol as the only product under controlled-irradiation conditions.

The differences in product distributions upon irradiation of compounds **1**, **2**, and **3** are ascribed to the different fragmentation rates of the C–X and S–benzyl bonds in the radical anion intermediates which arise from ET reactions from pinacolone enolate ion to the substrates. In this fashion, irradiation of **2** generates a radical anion which readily fragments to iodide ion and the respective aryl radical, which undergoes internal cyclization. Loss of a proton regenerates the radical anion of **9**, which in turn transfers the odd electron back to a substrate molecule **2** to continue the chain process. Conversely, the radical anions derived from **1** and **3** fragment into benzyl radicals and the respective sulfides, precluding the chain mechanism.

Product quantum yields were determined from irradiation of **1**, **2**, and **3** in the presence of pinacolone enolate ion, and are in accordance with the mechanisms proposed.

Introduction

The radical nucleophilic substitution reaction or $S_{RN}1$ is a well-documented process[1] which is widely proposed to include an initiation, a propagation, and a termination step in a cyclic fashion. The propagation cycle is depicted in eqns. (1)–(3).

$$(ArX)^{-\bullet} \longrightarrow Ar^{\bullet} + X^{-} \quad (1)$$

$$Ar^{\bullet} + Nu^{-} \longrightarrow (ArNu)^{-\bullet} \quad (2)$$

$$(ArNu)^{-\bullet} + ArX \longrightarrow ArNu + (ArX)^{-\bullet} \quad (3)$$

Few systems are known to react through a thermal (or spontaneous) $S_{RN}1$ reaction.[2] Most systems need to be initiated by other means. The most widely used method to initiate the chain process is photostimulation. Other methods that have been used are solvated electrons[3] or sodium amalgam in liquid ammonia,[4] reactions induced electrochemically,[5] by inorganic salts, such as Fe^{2+} salts[6] or by SmI_2.[7] Data are now available which characterise both the propagation cycle and the termination steps of this reaction.

Hoz and Bunnett attempted to characterise the mechanistic details of photoinitiation[8] in the reaction of PhI with diethyl phosphite ion. From quantum yield measurements, they could verify that photolysis was accomplished in one of three possible ways: i) homolytic cleavage of the C–I bond, ii) electron transfer (ET) from the anion to the excited PhI, bringing forth a radical anion that enters the cycle, or iii) electron exchange within an excited charge transfer complex (CTC), generating a species that allows entry in the propagation step. On the other hand, in the photostimulated reaction of 1-iodoadamantane with benzenethiolate ions, the mechanism of photoinitiation involves excitation of benzenethiolate ions with concomitant photoejection of electrons to the solvent. The reaction is not by a chain mechanism.[9]

Kornblum and co-workers[10] have determined the quantum yield for the $S_{RN}1$ substitution reaction of *p*-nitrocumyl chloride with azide ions (3.5), and quinuclidine (6000). Furthermore, by studying the wavelength dependence on the quantum yields, they have obtained evidence that the photochemical initiation proceeds by means of a CTC. Similar results have been obtained in the reaction of acetone enolate ion with PhI and PhBr in DMSO, whereas this is not the case when potassium diethyl phosphite is used as nucleophile.[11]

Acceleration of the substitution reaction of aryl halides with potassium diethyl phosphite or with 2-naphthoxide ions by potassium iodide has also been explained on the basis of an ET through the exciplex formed between the aryl halide and the iodide ions. It has also been reported[12] that iodide ions catalyze the photostimulated reaction of bromoarenes with diethyl phosphite ions.[13]

The photoinduced initiation reaction may have a low quantum yield, due to a fast backward ET which annihilates the ion pair before cage separation occurs. This will result in an inefficient source of radicals.

Thus, the magnitude of the chain length of any $S_{RN}1$ process can easily be derived from comparison of the quantum yield of the initiation step and an overall reaction quantum yield. It would therefore be possible to obtain quantum yields for the initiation step providing that the propagation and termination cyclic processes are eliminated or reduced significantly compared with the initiation step.

An attempt at "freezing" an $S_{RN}1$ reaction at the initiation level could be accomplished by designing a molecule where the propagation steps can be quenched by some other more efficacious process, such as an unimolecular process. That is, if the radical anion of the substitution product is an unstable

DOI: 10.1039/a908522j

Table 1 Reaction conditions and yields of products

Run	Substrate (Conc./10^{-3} M)	[**4**]/10^{-3} M	Photolysis/ min	Substrate[a] (%)	Products (%)[b]
1	**1** (8.04)	24.32	120[c]	99	**5** (0.1)
2	**1** (9.17)	27.50	20	96	**5** (2)
3	**1** (10.09)	26.90	30	91	**5** (5)
4	**1** (11.33)	28.20	120	85	**5** (10)[d]
5	**2** (31.00)	—	120	100	—
6	**2** (8.40)	24.12	120[c]	95	**9** (0), **10**–**11** (0)
7	**2** (15.40)	46.30	20	66	**9** (23), **10**–**11**(6)[e]
8	**2** (15.00)	46.00	45	11	**9** (39), **10**–**11** (27)[e]
9	**2** (9.64)	16.37	120[f]	0[g]	**9** (40), **10**–**11** (22)[e]
10	**2** (13.00)	0[g]	120[f]	60	**9** (7), **10**–**11** (2)[e]
11	**9** (17.90)	54.00	120	85	**10** (4), **11** (6)
12	**3** (10.26)	102.60	120[c]	90	**18** (—), **6** (—)
13	**3** (8.50)	25.50	15	95	**18** (1), **6** (1)
14	**3** (9.06)	22.65	30	82	**18** (4), **6** (9)

[a] Recovered substrate. [b] Determined by GLC using the internal standard method. [c] Dark conditions. [d] Product **6** was detected, but not quantified. [e] **10** and **11** were quantified together. The ratio of **10**:**11** was *ca.* 1:1. [f] Under these prolonged irradiation conditions, unidentified products were formed. [g] The base used was *t*-BuOK, 56 M × 10^{-3}.

species, which undergoes fragmentation rather than chain transfer (*i.e.* the unimolecular rate constant for fragmentation is much faster than the bimolecular rate constant for the ET chain).

The photostimulated reaction of phenylmethanethiolate ions with PhI yields only benzenethiolate ions, and no phenyl benzyl sulfide product is formed. The mechanism proposed is depicted in eqns. (4)–(7). Eqns. (4)–(6) constitute the propagation cycle

$$(PhI)^{-\bullet} \longrightarrow Ph^{\bullet} + I^{-} \quad (4)$$

$$Ph^{\bullet} + BnS^{-} \longrightarrow (Ph\text{–}S\text{–}Bn)^{-\bullet} \quad (5)$$

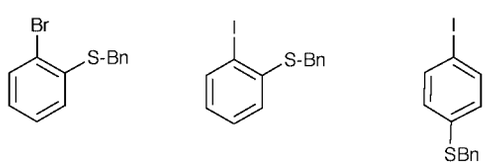
$$(Ph\text{–}S\text{–}Bn)^{-\bullet} + PhI \longrightarrow Ph\text{–}S\text{–}Bn + (PhI)^{-\bullet} \quad (6)$$

$$(Ph\text{–}S\text{–}Bn)^{-\bullet} \longrightarrow PhS^{-} + Bn^{\bullet} \quad (7)$$

of the $S_{RN}1$ mechanism. However, the radical anion intermediate formed in eqn. (5) fragments faster [eqn. (7)] than the intermolecular ET to the substrate can ensue. Benzyl radicals do not react with the nucleophile, they are reduced or dimerize instead.[14]

We believed that if an aromatic aryl radical bearing a substituent such as S–Bn, is made to react with a nucleophile, the resulting radical anion intermediate would fragment faster than ET to the substrate can ensue, and no propagation cycle would build up. The quantum yields would therefore represent only those of the initiation step.

We have therefore embarked on the syntheses of 1-bromo-2-[(phenylmethyl)thio]benzene (**1**), 1-iodo-2-[(phenylmethyl)-thio]benzene (**2**) and 1-iodo-4-[(phenylmethyl)thio]benzene (**3**) (Scheme 1). These three substrates could then be compared in

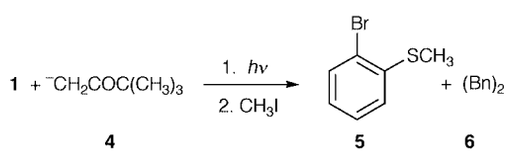


Scheme 1

their quantum efficiencies (initiation quantum yields) with the total quantum yields for analogues of iodobenzene (or PhI itself) in other $S_{RN}1$ reactions involving the same nucleophiles, on the premise that **1**, **2**, and **3** have similar or lower reduction potentials than those of the iodobenzenes to be investigated, and their quantum efficiencies (initiation) would resemble those of iodobenzenes (which cannot be measured directly).

Results and discussion

Pinacolone enolate ion (**4**) reacts under irradiation (1.5 h) with PhBr in DMSO to give 87% of the substitution product.[15] There is no dark reaction of substrate **1** with **4** (2 h), but upon irradiation, and subsequent quenching of the reaction with methyl iodide, products **5** and **6** are found [eqn. (8)], albeit in low yield (see Table 1). No bromide elimination or substitution products are detected in the photolysis mixture. These results are indicative of enolate **4** transferring one electron to **1** upon photostimulation, to yield the radical anion $\mathbf{1}^{-\bullet}$; fragmentation of the S–Bn bond as opposed to the C–Br bond ensues thereafter to afford *o*-bromobenzenethiolate ions (**7**) and benzyl radicals **8** [eqn. (9)]. Ion **7** is trapped by methyl iodide, and **8**



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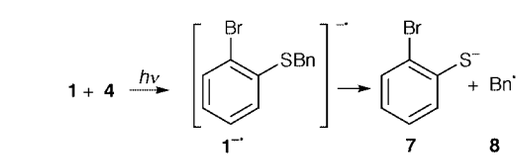
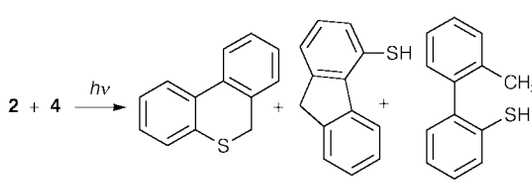


(9)

dimerizes to furnish products **5** and **6**, respectively. The fact that in this latter reaction the chain process is suppressed, results in an overall low reactivity.

As the frangibility of the C–I bond is greater than that of the C–Br bond in aromatic radical anions, we decided to investigate substrate **2** under similar reaction conditions. Direct photolysis (365 nm, 2 h) of substrate **2** in DMSO as solvent affords no reaction, but in the presence of **4**, under photostimulation (20 min), **9** is formed as the major product, along with small amounts of products **10** and **11** [eqn. (10), Table 1, run 7].

When the irradiation time is extended to 45 min, there is an increase in the yield of product **9**, with a concomitant increase

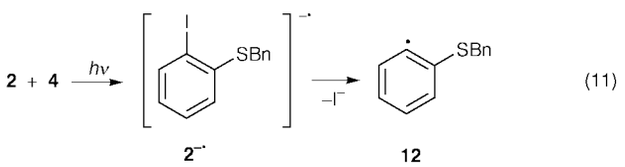


(10)

in the yields of products **10** and **11** (Table 1). Under longer irradiation times (2 h), substrate **2** reacts completely, but there is no further increase in the amounts of products **9–11**, and several minor products are formed. The photostimulated reaction (2 h) of **2** in the presence of *t*-BuOK as base did not lead to any significant accumulation of product(s).

The substitution product, (the one resulting from replacement of iodine by pinacolone enolate ion), or products derived from the S–Bn bond cleavage are not observed.

The formation of products **9–11** can be rationalized in terms of a photostimulated ET from **4** to **2** to form the radical anion $\mathbf{2}^{-\bullet}$ which undergoes fragmentation of the C–I bond to afford radical **12** and iodide ion [eqn. (11)]. Radical **12** has two possible reaction pathways, i) coupling with **4** to yield the radical anion of the substitution product $\mathbf{13}^{-\bullet}$ [eqn. (12)] which would ultimately give the substitution product **13**, or products from fragmentation of the S–Bn bond in $\mathbf{13}^{-\bullet}$, or ii) be trapped by the phenyl ring giving the radical adduct **14** [eqn. (13)].



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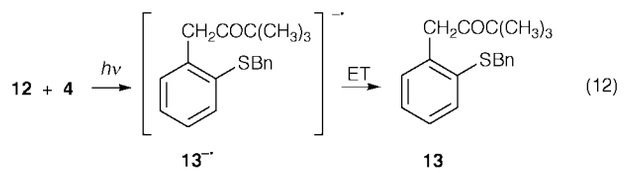

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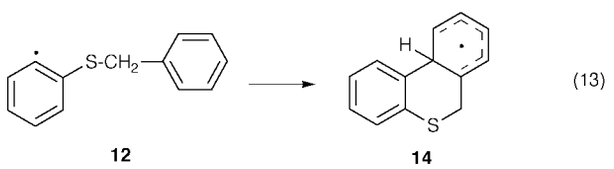

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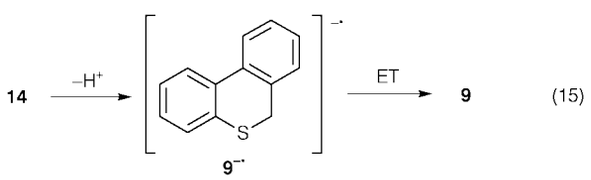


(15)

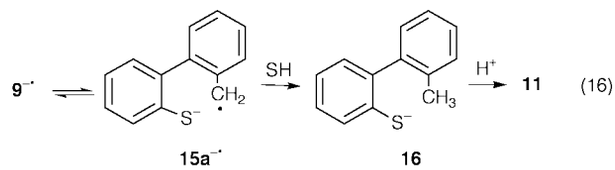
The substitution product **13**, or products from fragmentation of the S–Bn bond in $\mathbf{13}^{-\bullet}$ were not found in the reaction mixture, indicating that the rate of intramolecular cyclization of the radical to the benzene ring is much faster than the intermolecular reaction of radical **12** with nucleophile **4**. Trapping of aromatic radicals in the propagation cycle of the $S_{RN}1$ mechanism by aromatic rings is a documented process.[16]

Radical adduct **14** could traverse two different reaction pathways to achieve aromatization to finally afford **9**; *i.e.*, a hydrogen abstraction [eqn. (14)], or loss of a proton (by a base) to yield the radical anion $\mathbf{9}^{-\bullet}$ which by an ulterior ET to the substrate affords **9** [eqn. (15)].

The difference in both reactions is that eqn. (14) represents a termination step, whereas eqn. (15) is part of a chain process. To discriminate between both pathways we performed a quantum yield study, and found that the quantum yield for the disappearance of **2** is *ca.* 300, indicating that, indeed, a chain reaction is taking place (*vide infra*).

At short irradiation times (20 min) **9** is the major product, *ca.* 70% of reacting **2**, but after 45 min irradiation, products **10** and **11** increase in yields. To account for products **10** and **11**, radical anion $\mathbf{9}^{-\bullet}$ should undergo a ring opening reaction. Thus, the radical anion $\mathbf{9}^{-\bullet}$ can suffer C–S bond scission to afford the radical anion $\mathbf{15a}^{-\bullet}$ [eqn. (16)]. By hydrogen abstraction, radical $\mathbf{15a}^{-\bullet}$ gives the thiolate ion **16**, which ultimately affords product **11**, this being a termination step.

The C–C bond of the biphenyl moiety in $\mathbf{15a}^{-\bullet}$ ought to rotate to render intermediate radical anion $\mathbf{15b}^{-\bullet}$. The benzyl radical thus formed is trapped by the phenyl ring, affording the radical anion $\mathbf{17}^{-\bullet}$ [eqn. (17)].



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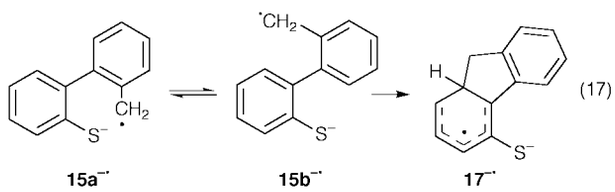


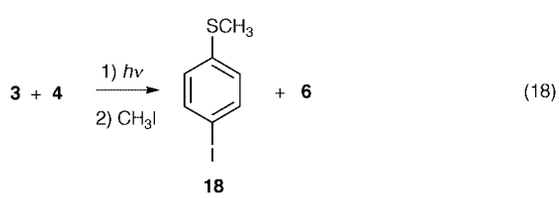
(17)

Radical anion $\mathbf{17}^{-\bullet}$ can lose a hydrogen, which will ultimately afford compound **10**.

The fact that at short irradiation times **9** is the main product, and on prolonged irradiation **10** and **11** become important, suggests that **9** is an intermediate in these reactions. When **9** is irradiated in the presence of **4**, products **10** and **11** are indeed formed, although in low yield, indicating that these two products are not formed in a chain process (Table 1, run 11).

Since a benzene ring in the *ortho*-position to the radical centre is trapped to yield a ring closure product much faster than coupling with the nucleophile can occur, we studied the isomeric *para*-substituted compound **3**.

There is no substitution product formed on reaction of **3** with **4** after two hours in the dark. Upon irradiation, *p*-iodobenzenethiolate (trapped by methyl iodide to render compound **18**) and product **6** are formed, although in overall low yields [eqn. (18)] (Table 1).



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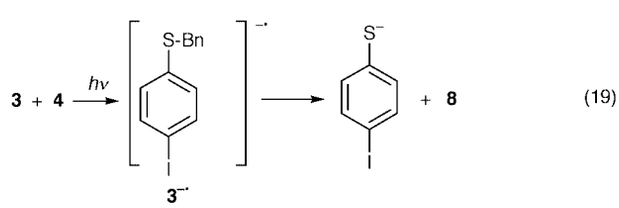


(19)

These results indicate that upon irradiation, **4** transfers one electron to **3** giving the radical anion intermediate $\mathbf{3}^{-\bullet}$; this latter suffers a S–Bn bond cleavage faster that the C–I bond fragmentation [eqn. (19)] can follow. Radicals **8** dimerize finally to afford **6**.

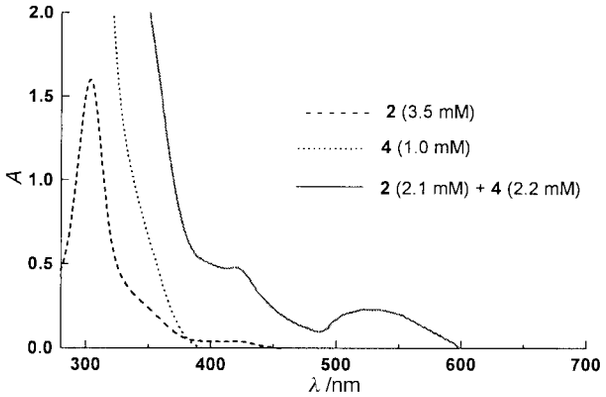


Fig. 1 UV-vis absorption spectra of **2** (----), **4** (·····) and **2** + **4** (——) in DMSO as solvent.

It is quite remarkable the different reaction pathways isomers **2** and **3** traverse, as we compare eqns. (10) and (18). As far as we know, there is no documented report on the change in fragmentation patterns in isomeric radical anions. In order to gain more insight, we have performed quantum yield determinations.

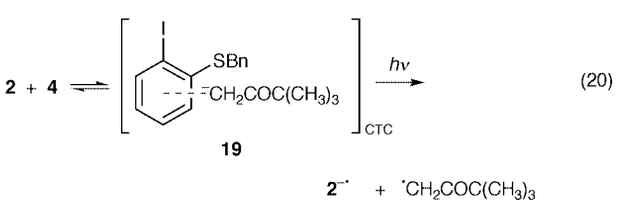
Quantum yield determinations

Evidence for complexation between substrate **2** and **4** is apparent upon bringing the reagents into contact. For instance, if a pale yellow deoxygenated solution of **4** in DMSO is mixed with a colourless deoxygenated solution of **2** in DMSO, an intense red–purple colour develops. The ultraviolet absorption spectra of the individual components and the mixture of **2** and **4** are shown in Fig. 1 ($\lambda_{\text{max complex}}$ = 521 nm).

The enhanced absorption, red-shifted into the visible and long wavelength UV spectral regions observed upon mixing the reagents, has been ascribed to the formation of a ground state CTC **19** [eqn. (20)], because the individual components of the reaction mixture can be recovered unchanged if the deep-red purple solutions are quenched by addition of dilute acid.

There seems not to be complexation between **4** and substrates **1** or **3** in the ground state. No fluorescence from pinacolone enolate ion, or in admixture with **1**–**3** was observed in DMSO as solvent.

That the reaction could possibly be triggered with complex-absorbed photons implies that some route exists from the excited complex to the propagation cycle [eqn. (20)].



(20)

Studies have shown that photoexcitation of CTCs (that are regarded as only slightly more stable than the free components) give rise to a non-relaxed state to which several fates are possible. Here, the one shown in eqn. (20) would be the most plausible; that is, ET within the complex.

It is suggested that ET within these CTCs would then be less important than alternate pathways available through direct irradiation, *e.g.*, initiation through **4** vertical excitation and ET to the substrate. Indeed, Fox *et al.*[11] postulated that the relative efficiencies for ET initiation within CTC might be predicted from the redox potentials of the component partners together with absorption band positions of the CTC.

Quantum yields were determined from the photoreaction of compounds **1**–**3** with **4** in 20 min of irradiation. Compounds **1** and **3** have quantum yields lower than unity; however, substrate **2** shows a quantum efficiency of *ca.* 300, based on substrate consumed, and a quantum yield of *ca.* 60 for the formation of **9**, and a quantum yield of *ca.* 35 for the formation of **10**–**11**. At short irradiation times (5 min), **2** affords **9** as the only photoproduct with a quantum efficiency of *ca.* 230 (see Table 2). Clearly substrates **1** and **3** photolyse in a nonchain reaction, whereas substrate **2** photolyses by a chain mechanism.

Table 2 Quantum yields (φ) from the photoreactions of **1**–**3** with **4** in DMSO at 365 nm[a]

Run	Substrate (Conc./ 10^{-3} M)	[**4**]/10^{-3} M	Chemical yield (%)	φ
1	**1** (9.17)	27.51	**1**[b] (96 ± 5)	0.18[c] ± 0.04
			5 (0.20 ± 0.005)	0.14 ± 0.03
2	**2** (11.9)	23.8	**2**[b] (61 ± 3)	298[c] ± 60
			9 (12 ± 0.6)	59 ± 10
			10 + **11** (7 ± 0.4)[d]	35 ± 7
3[e]	**2** (12.2)	29.3	**2** (91 ± 5)	248 ± 50
			9 (5 ± 0.2)	227 ± 45
4	**3** (7.87)	15.7	**3**[b] (96 ± 5)	0.81[c] ± 0.16
			18 (1.3 ± 0.6)	0.79 ± 0.15

[a] Conditions: Medium pressure Hg lamp unfiltered. Irradiation time: 20 min. Determined by ferrioxalate actinometry. All were run in duplicate parallel experiments and averaged two determinations each, unless otherwise indicated. [b] Substrate recovered. [c] Based on reacting substrate. [d] Ratio **10**:**11** *ca.* 1:1. [e] Irradiation time: 5 min λ irradiation 3500 Å in a Rayonet Reactor (2 lamps). Products **10** and **11** were not detected under these experimental conditions, and in duplicate parallel experiments and averaged two determinations each.

Conclusions

Whilst no $S_{RN}1$ substitution products were obtained, the fragmentation pattern of compounds **1**, **2**, and **3** show remarkable contrast. The radical ions of isomer **2** fragment through C–I bond scission whereas the radical anions of **1** and **3** do so by cleaving the S–Bn bond. This is, to the best of our knowledge, the first report where such photochemical behaviour is observed in two given isomers of a radical ion.

Experimental

General methods

Irradiations were conducted in a reactor equipped with two 400 W Hg lamps (Philips Model HPT, water-refrigerated) that emit maximally at 365 nm. Column chromatography was performed on silica gel (280 mesh). Gas chromatographic analyses were performed on a Hewlett-Packard 5890 Series II instrument with a flame ionisation detector, a Hewlett-Packard 3396 Series III integrator, and one of the following columns: HP1 5 m × 0.17 mm column, and a DB-1, 30 m × 0.17 mm column. ^{1}H NMR (200.133 MHz) and ^{13}C NMR (50.32 MHz) were conducted on a Bruker AC 200 spectrometer in deuterochloroform as solvent. Coupling constants (J) are given in Hz units. GC-MS analyses were carried out on a Perkin-Elmer GC-MS instrument employing a 30 m × 0.12 mm DB-1 column or on a Shimadzu GC-MS QP 5050 spectrometer equipped with a DB-5, 30 m × 0.18 mm id column. UV spectra were recorded on a Shimadzu 2100PC UV spectrometer. HRMS was run at McMaster Regional Centre for Mass Spectrometry, McMaster University, Canada.

Materials

1,4-Diiodobenzene, 1,2-diiodobenzene, benzenethiol, 2-bromobenzenethiol, *t*-BuOK, eicosane, silica gel, and benzyl chloride were all supplied by Aldrich Chemical Co. and used as received. Trimethyltin chloride and bis(triphenylphosphine)palladium dichloride were purchased from Strem Chemicals and used

as received. Phenanthroline, and iron trichloride were from Cicarelli. Pinacolone (Aldrich) was distilled and kept over dried molecular sieves (4 Å) until used. DMSO was received from Carlo Erba, and dried over molecular sieves (4 Å).

Photostimulated reaction of substrates 1–3 with pinacolone enolate ions in DMSO

The procedure is described in a previous publication.[1h] The actinometry was carried out at 365 nm (unfiltered medium pressure Hg lamp). The conversion of the actinometer (potassium ferrioxalate) was monitored by measuring the absorbance of the complex Fe–(*o*-phenanthroline) at 510 nm. A radiant power of *ca.* 4×10^{-9} einsteins s^{-1} was achieved after 20 min irradiation. The conversions of **1**–**3** were followed by gas chromatographic techniques. Product and substrate concentrations were determined relative to an internal standard (eicosane) and were corrected for relative FID response. The sample and the actinometer (duplicates) were placed equidistant to the lamp in a fixed arrangement. The preparation of the actinometer, potassium ferrioxalate $K_3Fe(C_2O_4)_3 \cdot 3H_2O$, was according to the protocol suggested by Hatchard and Parker.[17]

Syntheses

1-Iodo-2-[(phenylmethyl)thio]benzene (2)[18] and 1-iodo-4-[(phenylmethyl)thio]benzene (3).[19] General procedure. The palladium-catalyzed coupling of organotin compounds with carbon electrophiles, known as the Stille reaction,[20] has been shown to be a very important tool in organic synthesis. Many groups can be transferred. For instance, the catalyzed reaction of PhBr with Bu_3SnSBu affords PhSBu in 86% yield.[21] We decided to use this reaction to prepare substrates **2** and **3**. Into a 50 mL two-necked round bottom flask, equipped with a T-joint allowing for vacuum and N_2 inlets, a rubber septum, and a magnetic stir bar, 0.376 g (0.00303 mol) of phenylmethanethiol, and 0.519 g (0.0041 mol) of *t*-BuOK in 10.0 mL of DMSO were added. This solution was deoxygenated and blanketed three times with a N_2 atmosphere. To the resulting potassium phenylmethanethiolate pale yellow mixture, 0.886 g (0.00404 mol) of trimethyltin chloride were added. The solution was de-aerated and refilled with N_2 three times, and kept under a positive pressure. This constitutes solution "A". Into another 50 mL two-necked round bottom flask equipped with a water-cooled condenser, a vacuum/N_2 inlets, and a magnetic stir bar, diiodobenzene (*ortho*- or *para*-), 1.00 g (0.00303 mol), $PdCl_2(PPh_3)_2$, 0.111 g (0.000515 mol) in 18.5 mL DMSO were added. To this resulting deep yellow mixture, solution "A" was introduced slowly by syringe while stirring the mixture. The colour of the resulting mixture turned deep red. The admixture was again deoxygenated and blanketed with N_2 three times. The flask was left under a positive pressure of N_2 and immersed in an oil bath and kept at 100 °C for 5 hours. After the reaction time elapsed, and the temperature was brought down to ambient values, excess methyl iodide (0.007 mol) was introduced while stirring the mixture for an additional two hours. The reaction was finally quenched with doubly distilled water, ammonium nitrate was added, and extracted into ethyl ether three times. The ether extracts were washed with distilled water, and dried over anhydrous sodium sulfate, filtered, and the organic solvent evaporated using a rotary evaporator. The crude was chromatographed on silica gel column chromatography using petroleum ether (40–60 °C): dichloromethane 95 : 5 as mixture of elution solvents.

Product ***2*** was obtained in 68% isolated yield. NMR δ_H (200.133 MHz; $CDCl_3$; Me_4Si) 4.09 (2 H, s), 6.81 (1 H, octet $J_1 = 5.8$, $J_2 = 2.9$, $J_3 = 1.1$), 7.21 (7 H, complex m), 7.78 (1 H, dd, $J = 1.1$, 7.3). NMR δ_C (50.32 MHz; $CDCl_3$; Me_4Si) 39.14, 100.09, 127.05, 127.35, 128.29, 128.53, 128.94, 135.99, 139.45, 141.39. GC-MS EI, *m*/*z*: 326 ($M^{+\cdot}$, 60%), 235 (10), 197 (12), 165 (13), 108 (20), 91 (100), 82 (5), 65 (24), 51 (11), 39 (15), 32 (5).

Product ***3*** was obtained in 80% isolated yield. NMR δ_H (200.133 MHz; $CDCl_3$; Me_4Si) 4.05 (2 H, s), 6.97 (2 H, d, $J = 2.1$), 7.22 (5 H, br s), 7.51 (2 H, d, $J = 2.1$). NMR δ_C (50.32 MHz; $CDCl_3$; Me_4Si) 38.84, 91.20, 127.34, 128.56, 128.75, 131.42, 136.45, 136.99, 137.75. GC-MS EI, *m*/*z* 326 ($M^{+\cdot}$, 25%), 235 (10), 108 (12), 91 (100), 82 (2), 65 (25), 51 (10), 45 (5), 39 (8), 32 (3).

1-Bromo-2-[(phenylmethyl)thio]benzene (1). This compound was synthesised according to standard literature procedures, starting from potassium 2-bromobenzenethiolate and benzyl chloride in DMSO, 90% yield; mp 44–45 °C (from benzene). NMR δ_H (200.133 MHz; $CDCl_3$; Me_4Si) 4.18 (2 H, s), 7.06 (1 H, octet), 7.28 (7 H, complex m), 7.58 (1 H, br d). NMR δ_C (50.32 MHz; $CDCl_3$; Me_4Si) 37.92, 123.76, 126.46, 126.89, 127.27, 127.64, 128.53, 128.91, 132.90, 136.13, 137.81. GC-MS EI, *m*/*z* 280 ($M^{+\cdot}$, 5%), 278 (5),165 (2), 108 (6), 92 (5), 91 (100), 65 (10), 63 (4). HRMS 277.977100 ($C_{13}H_{11}BrS$ requires 277.976482).

Isolation and identification of the photoproducts. *6H-Benzo[c]thiochromene [230-04-6] (****9****).* This compound was isolated and purified (on silica gel, eluted with petroleum ether–diethyl ether (98 : 2)) from the photoreaction mixture. Its spectroscopic data agree well with those from a sample synthesised by an independent route.[22]

*2-Sulfanyl-2′-methyl-1,1′-biphenyl [87221-17-8] (****11****).* This compound was isolated and purified (on silica gel, eluted with petroleum ether–diethyl ether (98 : 2)) from the photoreaction mixture, and characterised by spectroscopic data, which match those reported in the literature.[23] GC-MS EI, *m*/*z* 200 ($M^{+\cdot}$, 100%), 184 (95), 185 (100), 165 (10), 152 (43), 139 (15), 115 (2), 89 (1), 77 (4), 63 (5), 51 (13), 39 (17), 32 (23).

*1-Iodo-4-methylthiobenzene [230-04-6][24] (****18****).* This compound was isolated and purified (on silica gel, eluted with petroleum ether–diethyl ether (98 : 2)) from the photoreaction mixture. Its spectroscopic data agree well with those from a sample synthesised from an independent route.

*9H-Fluorene-4-thiol [90590-03-7][25] (****10****).* Isolated as a white solid after radial chromatography on silica gel, eluted with petroleum ether–diethyl ether (98 : 2). NMR δ_H (200.133 MHz; $CDCl_3$; Me_4Si) 3.80 (2 H, s), 7.23 (4 H, complex m), 7.42 (2H, br d), 7.68 (1H, br d). GC-MS EI 198 ($M^{+\cdot}$, 65%), 197 (100), 171 (2), 165 (24), 152 (12), 63 (2).

*1-Bromo-2-methylthiobenzene [19614-16-5] (****5****).* Isolated as a white solid after radial chromatography on silica gel, eluted with petroleum ether–diethyl ether (98 : 2). The spectroscopic data agree well with those reported in the literature.[26]

Acknowledgements

This work was supported in part by the Consejo de Investigaciones de la Provincia de Córdoba (CONICOR), the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), SECYT, Universidad Nacional de Córdoba and FONCYT, Argentina.

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Paper a908522j