Reactions of *o*-iodohalobenzenes with carbanions of aromatic ketones. Synthesis of 1-aryl-2-(*o*-halophenyl)ethanones

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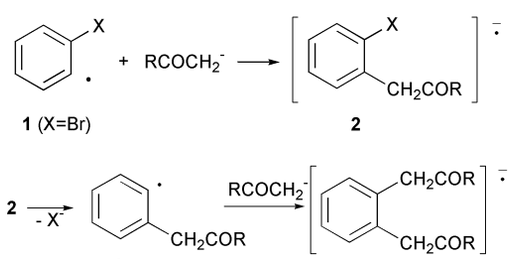
Received (in Cambridge, UK) 18th February 2002, Accepted 2nd April 2002
First published as an Advance Article on the web 26th April 2002

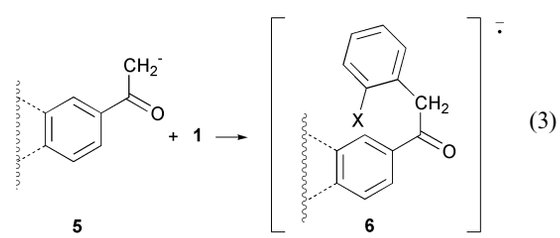
o-Iodohalobenzenes (X = I, Br, Cl) react in DMSO with the enolate ions of acetophenone, propiophenone and 1-(2-naphthyl)ethanone to afford mainly monosubstitution with retention of one halogen. The monosubstituted dehalogenated compounds are formed in low overall yields in the reactions of *o*-diiodobenzene with the carbanions of 1-(2-naphthyl)ethanone and of acetophenone and in the reaction of *o*-bromoiodobenzene with the carbanion of propiophenone. The reactions can be performed in the dark, with usually increased yields of substitution under irradiation, as well as under $FeBr_2$ initiation. Treatment of 2-(2-bromophenyl)-1-phenylethanone with Cu bronze affords the ring closure benzofuran product. The degree of dehalogenation is discussed in terms of the energetics of the intramolecular electron transfer (ET) from the ArCO-π system to the C–halogen σ bond in the monosubstituted radical anions proposed as intermediates. The lack of ring closure of the radicals formed by dehalogenation of these radical anions is analyzed in terms of geometric factors.

The aromatic radical nucleophilic substitution, or $S_{RN}1$ reaction, has been shown to be an excellent route to perform the nucleophilic substitution of unactivated aromatic compounds with suitable leaving groups.[1] Although the carbanions of aliphatic ketones are efficient nucleophiles in these reactions, the enolates of aromatic ketones as the anion of acetophenone[2] and derivatives[3] have a low reactivity toward halobenzenes or halonaphthalenes under irradiation in liquid ammonia. The heteroarylation of the enolate of acetophenone is possible in this solvent under irradiation[4,5] and even in the dark,[6] but with π-electron deficient heteroaromatic halides and with aryl diazosulfides.[7] However, phenylation by phenyl halides has succeeded under photoinitiation in DMSO.[8] The difference in reactivity between enolate anions of aromatic and aliphatic ketones toward phenyl halides in liquid ammonia has been attributed to the lower efficiency of the former in the photoinitiated electron transfer (ET) step of the proposed mechanism.[8,9]

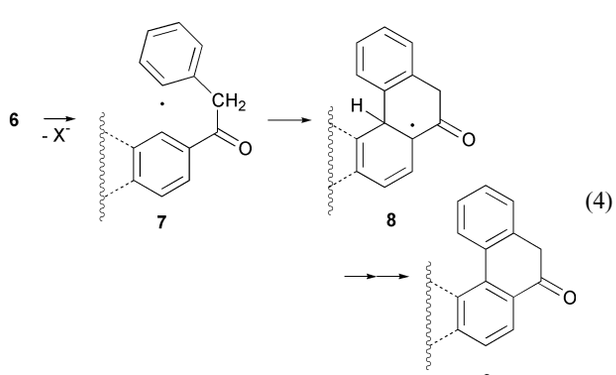
In the reaction of *o*-dibromobenzene with the enolate ion of pinacolone, mainly disubstitution (62%) is obtained.[10] When the reaction is performed with the anion of acetone, cyclic compounds from an aldol condensation of the disubstitution product are formed (≈64%).[10] In this reaction, it is proposed that the *o*-bromophenyl radical **1**, formed by fragmentation of the radical anion of *o*-dibromobenzene, couples with the nucleophile to afford the monosubstituted radical anion **2** [eqn. (1)]. This intermediate can fragment at the second C–Br bond to give radical **3**, which is able to react with the nucleophile to form the radical anion of the disubstitution product **4** [eqn. (2)].

The C–halogen fragmentation of radical anion **2** depends mainly on the type of halide and nucleophilic moieties present as well as on their relative position in the phenyl ring.[1] We consider the study of the preferred reaction path followed by *o*-iodohaloarenes with enolate ions of aromatic ketones **5** to be of interest. In this system intermediate **6** could be formed [eqn. (3)].



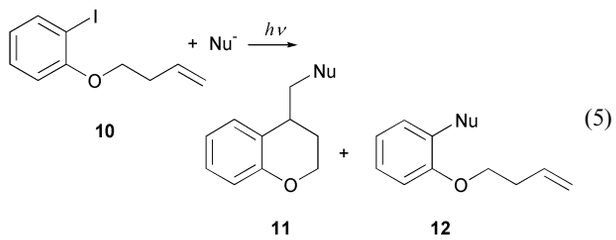


Monosubstitution with retention of halide will be obtained if the fragmentation reaction of the C–halogen bond of this intermediate is not favoured. On the other hand, if the bond does fragment, radical **7** will be formed [eqn. (4)]. This radical can couple with the nucleophile to afford disubstitution (a probably unfavourable reaction due to steric constraints in the case of aromatic enolates). Another possibility for radical **7** is to form the reduced product by hydrogen abstraction from the solvent or, more interestingly, to be trapped by the aryl ring of the nucleophilic moiety to afford finally the cyclized product **9** [eqn. (4)].



 DOI: 10.1039/b201692c

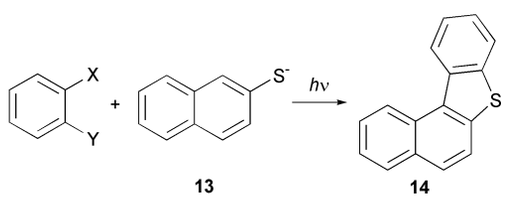
The $S_{RN}1$ mechanism offers the possibility to obtain ring closure compounds by trapping of the radicals, formed along the propagation cycle, with adequate reactive centers.[1] For example, in the reaction of the radical probe *o*-(but-3-enyloxy)iodobenzene **10** with different nucleophiles, both the cyclized and straightforward substitution products were formed in yields that depend on the nucleophile used. For instance, the reaction with PhS^- ions gave **11** (Nu = SPh) and **12** (Nu = SPh) in 76 and 6% yields, respectively [eqn. (5)].[11]



(5)

Formation of compound **11** is ascribed to the trapping of the aryl radical by the double bond of the but-3-enyloxy chain to afford a cyclic primary alkyl radical which by reaction with PhS^- finally yields **11** (Nu = PhS).

Another known process is the trapping of the radical centre by the π-system of an aromatic ring.[12] For example, *o*-dihalobenzenes react with naphthalene-2-thiolate ions **13** to give the cyclic product **14** as indicated in eqn. (6).[13,14]



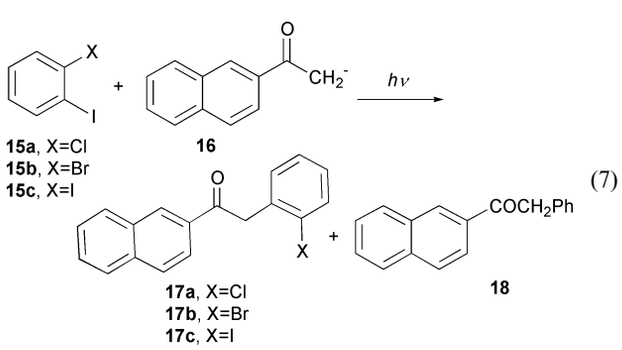
(6)

In order to determine the preferred path followed in our system, mainly focused on the possibility of achieving the synthesis of cyclic compounds of type **9**, we studied the reaction of the enolates of acetophenone, propiophenone and 1-(2-naphthyl)ethanone with *o*-iodohalobenzenes in DMSO. Theoretical calculations to elucidate the reactivity of the radical anions proposed as intermediates as well as the geometric properties of the monosubstituted dehalogenated radicals formed under our experimental conditions are presented at the UHF/AM1 level.

Results

Enolate ions of 1-(2-naphthyl)ethanone (16)

It is known that the enolate ion **16** reacts with iodobenzene in DMSO under irradiation[15] (for the results obtained under our experimental conditions see Table 1, expt. 1), or $FeCl_2$ initiation[16] to afford 1-(2-naphthyl)-2-phenylethanone. In the photoinitiated reaction of **16** with **15a**–**c**, the substitution products with retention of halogen **17a**–**c** were obtained (71, 86 and 50% yields respectively) [eqn. (7), Table 1, expts. 2, 3, 7].



(7)

The substitution of **15b** can be achieved in the dark (Table 1, expt. 5); similar behavior has previously been reported for the reaction of some ketone enolate ions with good electron acceptors aromatic halides, either in DMSO or in liquid ammonia.[17] Both the photoinitiated and the dark reactions are inhibited by *p*-dinitrobenzene (*p*-DNB), a well known scavenger of the $S_{RN}1$ mechanism (Table 1, expts. 4, 6).

The monosubstituted dehalogenated compound **18** is not formed in the reaction with **15a**,**b** but it is obtained in 17% yield with **15c** (Table 1, expt. 7). Fig. 1 shows the results afforded by

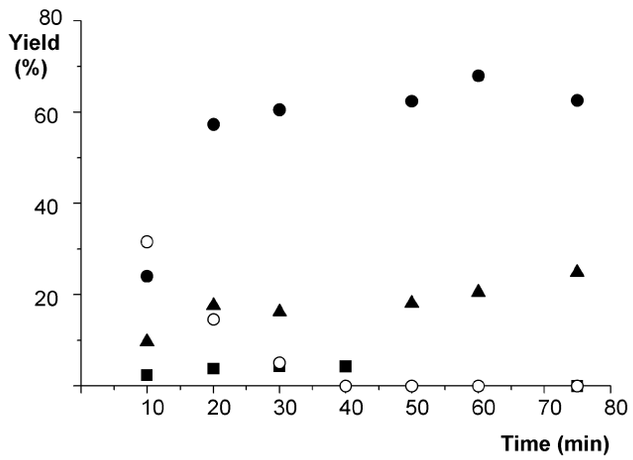


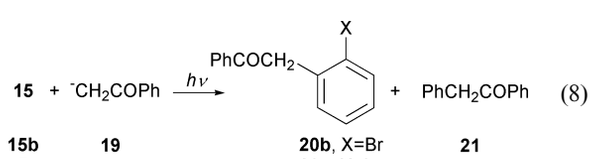
Fig. 1 Product and substrate relationship obtained by sampling the reaction of **16** with **15c** at different irradiation times. PhI (■); **15c** (○); **17c** (●); **18** (▲).

sampling the reaction at different irradiation times. As can be seen from Fig. 1 both compounds **17c** and **18** are formed simultaneously, indicating that **17c** is not an intermediate in the formation of **18**.

The product distribution of the latter reaction varies with the nucleophile : substrate ratio (Table 1, expts. 7, 8). Under shorter irradiation times and with a 5-fold excess of nucleophile, the percentage of **18** increases to 31% accompanied by 47% of **17c** (Table 1, expt. 8). On the other hand, only traces of **18** are formed when the reaction of **16** with **15c** is initiated with $FeBr_2$; the main product being **17c** (65% yield, Table 1, expt. 9).

Acetophenone and propiophenone enolate ions

In the photoinitiated reaction of the enolate ion of acetophenone (**19**) with *o*-bromoiodobenzene (**15b**), the monosubstituted compound with retention of bromine **20b** is formed uncontaminated by the monosubstituted dehalogenated product **21** (Table 1, expt. 10) [eqn. (8)]. The percentage of **20b** increases when a 6-fold excess of **19** is employed (76–88%) but not under $FeBr_2$ initiation (Table 1, expts. 11–13).



(8)

On the other hand, **20c** and **21** are formed in the reaction of **19** with *o*-diiodobenzene (**15c**) after 60 min of irradiation (Table 1, expt. 14). The ratio **20c** : **21** remains constant as shown by sampling the reaction at different irradiation times (Fig. 2).

It is known that **20b** reacts in DME with Cu (activated copper bronze)[18] to give the cyclic product 2-phenylbenzofuran **22**. In order to obtain this compound we performed the reaction of **15b** with **19** in DMSO. After 60 min of irradiation Cu was added and after 24 h at 50 °C, **20b** was the only product obtained (Table 1, expt. 12). Even though this *one-pot* approach

Table 1 Photostimulated[a] reaction of *o*-dihalobenzene with carbanions in DMSO

Expt.	Substrate (10^3 M)	Nu^- (10^3 M)	*t*-BuOK/10^3 M	Y[b]	ArX[c]	NuAr[c]	NuArX[c]
1	C_6H_5I (36)	**16** (145)	162	75		80	
2	*o*-C_6H_4ClI (41)	**16** (143)	156	I = 90	Nq		X = Cl, 71
3	*o*-C_6H_4BrI (39)	**16** (156)	170	I = 81	X = Br, <1		X = Br, 86
4[d]	*o*-C_6H_4BrI (27)	**16** (66)	77	I = 65	X = Br, 31		X = Br, 33
5[e]	*o*-C_6H_4BrI (21)	**16** (58)	75	I = 53	X = Br, 24		X = Br, 31
6[e,f]	*o*-C_6H_4BrI (21)	**16** (61)	67	I < 10			
7	*o*-$C_6H_4I_2$ (26)	**16** (69)	128	155	X = I, 1	17	X = I, 50
8[g]	*o*-$C_6H_4I_2$ (19)	**16** (96)	142	135	X = I, 1	31	X = I, 47
9[h]	*o*-$C_6H_4I_2$ (26)	**16** (159)	209			1	X = I, 65
10	*o*-C_6H_4BrI (39)	**19** (75)	90		X = Br, 15		X = Br, 44
11[i]	*o*-C_6H_4BrI (39)	**19** (217)	245	I = 89	X = Br, 14		X = Br, 76
12[j,k]	*o*-C_6H_4BrI (34)	**19** (202)	323				X = Br, 88
13[h]	*o*-C_6H_4BrI (34)	**19** (202)	263				X = Br, 54
14[j]	*o*-$C_6H_4I_2$ (26)	**19** (230)	332	181		25	X = I, 19
15[g]	1-Br-2-$IC_{10}H_6$ (20)	**19** (173)	199		X = Br, 2	20	X = Br, 59
16[l]	*o*-C_6H_4BrI (50.6)	**26** (500)	610	—	X = Br, 25	10	X = Br, 48
17[e]	*o*-C_6H_4BrI (50.6)	**26** (500)	550	I = 100 Br = 10	X = Br, 11	9	X = Br, 35
18[m]	*o*-C_6H_4BrI (52.0)	**26** (520)	572	I = 86 Br = 5	X = Br, 34	4	X = Br, 46
19	*o*-C_6H_4BrI (50.6)	**26** (500)	600	I = 100 Br = 21	X = Br, 44	28	X = Br, 2

[a] Irradiation time = 180 min, unless otherwise indicated. [b] Percentage of halogen quantified potentiometrically on the basis of the substrate concentration. [c] Quantified by GLC using the internal standard method. [d] *p*-Dinitrobenzene (38 mol%). [e] Dark reaction. [f] *p*-Dinitrobenzene (48 mol%). [g] Irradiation time = 120 min. [h] $FeBr_2$ (80 mol%). Reaction time = 30 min. [i] Irradiation time = 90 min. [j] Irradiation time = 60 min. [k] After irradiation Cu = 2.24 mmol (220 mol%) was added and the reaction heated at 50 °C for 24 h. [l] $FeBr_2$ (90 mol%). Reaction time = 90 min. [m] Irradiation time = 30 min.

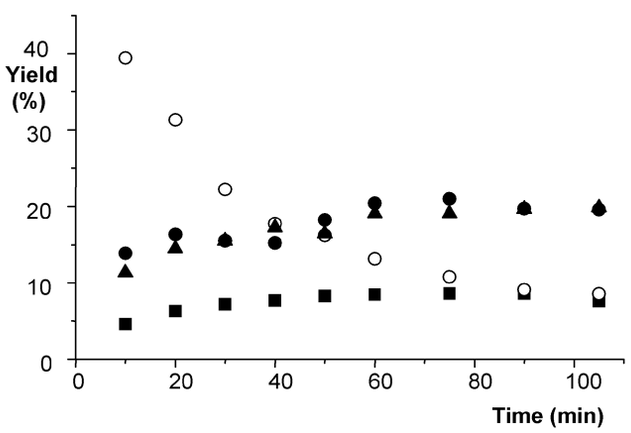
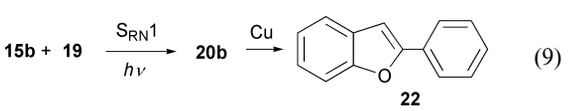


Fig. 2 Product and substrate relationship obtained by sampling the reaction of **19** with **15c** at different irradiation times. PhI (■); **15c** (○); **20c** (●); **21** (▲).

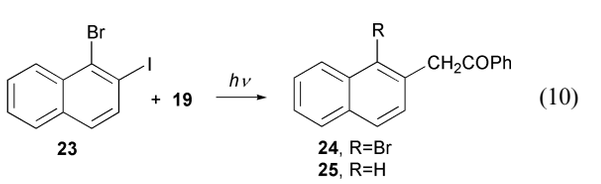
failed, compound **22** was obtained in 62% yield after treatment of **20b**, an isolated sample, with copper bronze [eqn. (9)] in



(9)

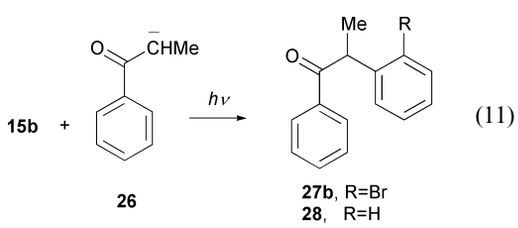
DME. Compound **22** is also obtained although in low yields (10%) by irradiation of **20b** in DMSO (λ_{max} = 253 nm, 60 min).

The monosubstituted **24** and monosubstituted-dehalogenated **25** are formed by reaction of 1-bromo-2-iodonaphthalene (**23**) with **19** (59 and 20% yield respectively) [eqn. (10)], Table 1, expt. 15).



(10)

The enolate ion of propiophenone (**26**) reacts with **15b** under $FeBr_2$ initiation to afford PhBr (25%), **27b** (48%) and **28** (10%) [eqn. (11), Table 1, expt. 16]. A similar product distribution is



(11)

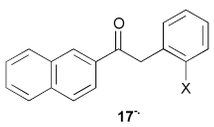
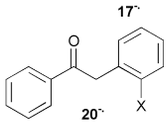
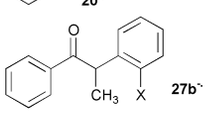
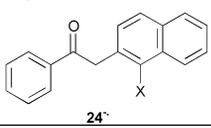
obtained when the dark reaction is performed in the absence of $FeBr_2$ as well as under short irradiation times (30 min) (Table 1, expts. 17, 18).

Sampling of the irradiated reaction at different reaction times shows that the concentration of **28** increases to 28% after 3 h. Moreover, when **27b** is treated with excess *t*-BuOK under irradiation (60 min) in the presence of the enolate ion **26**, compound **28** is formed (14%). Thus, the anion of the halo-monosubstituted product, formed in the basic medium can account for approximately 14% of the formation of **28** but only after prolonged irradiation times. This pathway has been disregarded on experimental grounds for the bromo derivative **20b**.[19]

Discussion

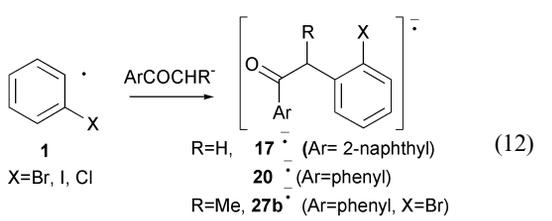
The mechanism of formation of the monosubstituted compounds **17**, **20** and **27b** is straightforward. Once **15** receives an electron, the radical anion formed fragments at the C–I bond to afford radicals **1** which can be reduced to the halobenzene (5–15% by reaction with anions **16** or **19** and 25–34% with anion **26**) or can couple with the enolates of the aromatic ketones to give the monosubstituted radical anions $\mathbf{17}^{-\bullet}$, $\mathbf{20}^{-\bullet}$ or $\mathbf{27b}^{-\bullet}$. It is known that the radical–nucleophile coupling reaction competes with the radical–hydrogen atom abstraction from enolate ions bearing β-hydrogens.[20] This explains the high yields of PhBr formed with anion **26**. Similarly, PhBr (93%) and traces of substitution product are formed in the irradiated

Table 2 AM1 calculated heats of formation and C–X bond lengths for radical anions $17^{-\bullet}$, $20^{-\bullet}$, $27b^{-\bullet}$ and $24^{-\bullet}$

Radical anion (RA)	X	r(C–X)/Å		Δ_fH/kcal mol^{-1}		$\Delta E_{\sigma-\pi}$/kcal mol^{-1}
		RAπ	RAσ	RAπ	RAσ	
	Cl	1.710	1.989	−9.6	12.0	21.6
	Br	1.883	2.077	2.5	14.9	12.4
	I	2.030	2.167	13.4	22.9	8.8
	Br	1.883	2.078	−8.7	−1.4	7.3
	I	2.029	2.169	2.8	6.1	3.6
	Br	1.886	2.078	−9.77	−4.0	5.8
	Br	1.888	2.065	9.1	12.7	3.6

reaction of the enolate ion of isobutyrophenone with *o*-bromoiodobenzene (**15b**) and in the reaction of the carbanion derived from **21** with o-diiodobenzene (6% of 1,2,2-triphenylethanone and ≅50% of PhI).

The radical anions formed in the coupling afford the monosubstituted compounds **17**, **20** or **27b** by ET to the substrate [eqn. (12)] or can fragment at the C–halogen bond to afford radicals **29** [eqn. (13)].



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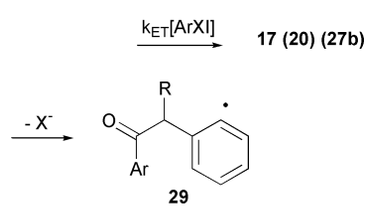


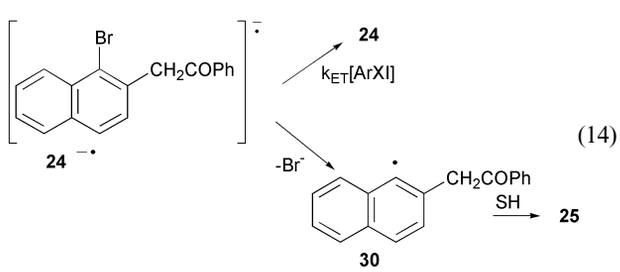
(13)

Based on our experimental results, the intermolecular ET [eqn. (12)] is the main reaction of all the radical anions formed. The fragmentation of the C–X bond [eqn. (13)] is only in play for intermediates $\mathbf{17c}^{-\bullet}$, $\mathbf{20c}^{-\bullet}$ (X = I, R = H) and $\mathbf{27b}^{-\bullet}$ (R = Me, X = Br) as indicated by the formation of the monosubstituted-reduced products.

Table 2 lists the heats of formation and electronic properties of radical anions $\mathbf{17}^{-\bullet}$, $\mathbf{20}^{-\bullet}$, and $\mathbf{27b}^{-\bullet}$, determined theoretically with the semiempirical AM1/UHF method as implemented in AMPAC.[21,22] In agreement with previous reports, these intermediates display π–σ electronic isomerism;[23,24] the unpaired spin distribution in the most stable radical anions is localized in the π-system of the arylcarbonyl group, which is separated from the *o*-haloaryl moiety by an sp^3 carbon atom. The energy difference between the π and the σ species, which has an elongated C–halogen bond in which the unpaired electron is located,[25] has been proposed as an indication of the feasibility of the intra-ET reaction between both electronic systems and thus of the relative order of their fragmentation rates.[23b,c]

As can be seen from the values of $\Delta_fH_{\sigma-\pi}$ presented in Table 2, in these radical anions the intra-ET from a given π arylcarbonyl system, for example Ar = 2-naphthyl, to the σ C–halogen bond of the 2-halophenyl substituent is favoured in the order Cl < Br < I. When X = I, the intra-ET is more favourable for $\mathbf{20c}^{-\bullet}$ (Ar = PhCO) than for $\mathbf{17c}^{-\bullet}$ (Ar = 2-naphthylCO) (Table 2), in agreement with the experimental findings. According to our calculations, the intra-ET from the 2-naphthylCO to the 2-iodophenyl moieties in $\mathbf{17c}^{-\bullet}$ and the intra-ET from the PhCO to the 2-bromophenyl moieties in $\mathbf{20b}^{-\bullet}$ have similar thermodynamics but the reaction was experimentally observed only for X = I.

In the case of the bromo derivatives formed by coupling with the enolates of propiophenone and acetophenone, both the experimental results and the theoretical thermodynamics show a slightly favoured intra-ET for $\mathbf{27b}^{-\bullet}$ with respect to $\mathbf{20b}^{-\bullet}$ The studies also indicate that the intra-ET is possible in $\mathbf{24}^{-\bullet}$, that is, from the PhCO moiety to the C–Br bond of the 2-bromonaphthyl system, as indicated by the formation of **25** in the reaction of **19** with **23** [eqn. (14)]. In intermediate $\mathbf{24}^{-\bullet}$ the



(14)

electron affinity of the bromoaryl acceptor moiety is increased with respect to that of the bromophenyl system of $\mathbf{20b}^{-\bullet}$ due to the presence of the naphthyl π-system.

The main difference between the intermediates formed by coupling of radical **1** with enolates of aromatic and aliphatic ketones [eqn. (1)] is that while in the former the most stable radical anions have the unpaired spin at the π ArCO system, in the latter, for example in the case of $\mathbf{2}^{-\bullet}$ [eqn. (1), R = $C(Me)_3$], the unpaired spin is located at the phenyl ring of the 2-bromophenyl moiety, which is more stable than the π-system of the C=O group. This radical anion behaves more like a bromobenzene radical anion which has been determined to fragment with a rate close to diffusion.[26]

Another result to point out is that the radicals **29** and **30** formed by fragmentation of the C–X bond [eqns. (13), (14)] neither react further with the nucleophile to afford disubstitution nor are trapped by the aromatic ring or the oxyanion centre to afford cyclic compounds.

The conformational potential surface of these radicals was determined as a function of the main dihedral angles C_4–C_3–C_2–C_1 and C_3–C_2–C_1–C_5 as indicated in Fig. 3.

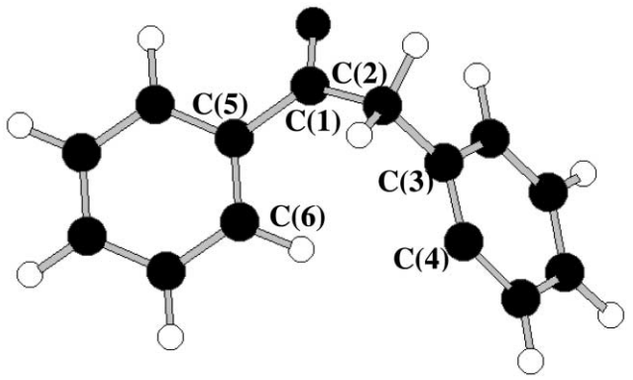


Fig. 3 AM1/UHF most stable conformation of the radicals formed by C–halogen cleavage of the radical anion intermediates.

Four conformers were located as minima on the potential surface, the most stable being in all cases the conformer shown in Fig. 3 and this is taken as representative. In this conformer the radical centre is twisted from the π molecular plane of the enolate system. Furthermore, the C_4–C_6 distance (3.6–3.7Å) is slightly longer than the distance of 2.97 Å calculated between the reacting centres that afford compound **14** [eqn. (6)]. This geometrical disposition could be one of the factors that kinetically disfavours the trapping of the radical centre by the aromatic ring of the ketone moiety and thus the ring closure reaction.

Conclusions

We have determined experimentally that the main reaction pathway followed by the enolates of the aromatic ketones acetophenone, propiophenone and 1-(2-naphthyl)ethanone with *o*-iodohalobenzenes in DMSO under ET conditions is monosubstitution with halide retention. Even though the monosubstituted dehalogenated radicals are formed mainly by reaction with *o*-diiodobenzene, these radicals do not react with the aromatic ring of the ketone to afford ring closure products. The results reported present an unexpected behaviour for *o*-dihalobenzenes for which the most common reaction under $S_{RN}1$ conditions is usually disubstitution or monosubstitution with dehalogenation. The reactions here presented are thus an interesting route to 1-aryl-2-(*o*-haloaryl)ethanones which can be converted to 2-substituted benzofuran derivatives by treatment with Cu bronze as shown for **20b** or under catalysis by other transition metals.[27]

Experimental

General

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 200 MHz nuclear magnetic resonance spectrometer with $CDCl_3$ as solvent. Infrared spectra were recorded on a Nicolet FTIR 5-SXC spectrophotometer. Gas chromatographic analyses were performed on a Hewlett Packard 5890 Series II with a flame-ionization detector and the data system Hewlett Packard 3396 Series II integrator, on a HP-1 capillary column (methyl silicone, 10 m × 0.53 mm × 2.65 μm film thickness). The GC-MS analyses were carried out on a Shimadzu GC-MS QP 5050 spectrometer, employing a 30 m × 0.12 mm DB-5 MS column. HRMS spectra were recorded at the Microanalysis Service and the Mass Spectrometry Laboratory of the *Centro de Investigación y Desarrollo* (C.I.D.), C.S.I.C., Barcelona, Spain. Column chromatography was performed on silica gel (70–270 mesh ASTM). The distillation at reduced pressure was performed with a Kügelrohr apparatus. Irradiation was performed in a reactor equipped with two 400 W lamps with maximum emission at 350 nm (Philips Model HPT, air- and water-cooled). Potentiometric titration of halide ions was performed with a pH meter using an Ag/Ag^+ electrode. Melting points were not corrected.

Materials

Potassium *tert*-butoxide, *o*-diiodobenzene, *o*-bromoiodobenzene, *o*-bromochlorobenzene and propiophenone were commercially available and used as received. DMSO was distilled under vacuum and stored under molecular sieves (4 Å). 1-Bromo-2-iodonaphthalene was prepared by reaction of potassium iodide with 2-bromonaphthalene-l-diazonium salt as described elsewhere.[28] Acetone and acetophenone were distilled and stored on molecular sieve (4 Å). 1-(2-Naphthyl)ethanone was recrystallized from petroleum ether.[29]

Photostimulated reaction of enolate ions of 1-(2-naphthyl)-ethanone (16) with *o*-diiodobenzene

The following procedure is representative. The reactions were carried out in a 100 mL three-necked round-bottomed flask equipped with a nitrogen inlet and magnetic stirrer. To 40 mL of dry and degassed DMSO under nitrogen were added 8.0 mmol of potassium *tert*-butoxide and 4.8 mmol of **16**. After 15 min *o*-diiodobenzene (1.5 mmol) was added and the reaction mixture was irradiated for 180 min. The reaction was quenched with an excess of ammonium nitrate and water (120 mL). The mixture was extracted twice with methylene chloride (40 mL), the organic extract was washed twice with water, dried, and quantified by GLC. The iodide ions in the aqueous solution were determined potentiometrically.

The solvent was removed under reduced pressure. The residue after column chromatography on silica gel [petroleum ether–diethyl ether (95 : 5)] gave 2-phenyl-1-(2-naphthyl)-ethanone (**18**) [mp 98–99 °C (lit.[30] mp. 99–99.5 °C). ν_{max}/cm^{-1} 1677 (CO). δ_H 2.35 (2H, s, CH_2), 7.0–8.2 (12H, m)] and 2-(2-iodophenyl)-1-(2-naphthyl)ethanone (**17c**) contaminated with nucleophile. This mixture was distilled under reduced pressure in the Kügelrohr.

2-(2-Iodophenyl)-1-(2-naphthyl)ethanone (17c). Found: M^+, 372.0020. $C_{18}H_{13}IO$ requires 372.0011. ν_{max}/cm^{-1}1683 (CO). δ_H 4.6 (2H, s, CH_2); 6.9–7.1 (1H, m); 7.2–7.7 (5H, m); 7.8–8.2 (4H, m); 8.6 (1H, s). *m*/*z* 372 (M^+, 2%), 332 (2), 331 (2), 247 (0.2), 246 (33), 245 (11), 157 (1), 156 (13), 155 (100), 128 (3), 127 (22).

2-(2-Bromophenyl)-1-(2-naphthyl)ethanone (17b). Mp 113–114 °C. Found: M^+, 324.0153 and 326.0134. $C_{18}H_{13}BrO$ requires 324.0150. ν_{max}/cm^{-1}1683 (CO). δ_H 4.6 (2H, s, CH_2); 7.1–7.7 (6H, m); 7.8–8.2 (4H, m); 8.6 (1H, s). *m*/*z* 327 (0.4), 326 (M^+, 1.4%), 325 (0.4), 324 (M^+, 1.5), 246 (1), 245 (3), 157 (1), 156 (12), 155 (100), 128 (2), 127 (22).

2-(2-Chlorophenyl)-1-(2-naphthyl)ethanone (17a). mp 109–110 °C. Found: M^+, 280.0652 and 282.0637. $C_{18}H_{13}ClO$ requires 280.0655. ν_{max}/cm^{-1} 1683 (CO). δ_H 4.6 (2H, s, CH_2); 7.1–7.7 (6H, m); 7.8–8.2 (4H, m); 8.6 (1H, s). *m*/*z* 283 (0.3), 282 (M^+, 1.3%), 281 (0.8), 280 (M^+, 3.1), 247 (0.3), 246 (0.5), 245 (2), 157 (1), 156 (13), 155 (100), 128 (3), 127 (25).

2-(2-Bromophenyl)-1-phenylethanone (20b). Mp 68–69 °C (lit.[31] 69.5–70 °C). ν_{max}/cm^{-1}1683 (CO). δ_H 4.5 (2H, s, CH_2); 7.0–7.7 (7H, m); 7.95–8.15 (2H, m). *m*/*z* 196 (1), 195 (M − Br, 15%), 106 (8), 105 (100), 89 (8), 78 (3), 77 (51).

2-(2-Iodophenyl)-1-phenylethanone (20c). ν_{max}/cm^{-1}1683 (CO). δ_H 4.5 (2H, s, CH_2); 6.9–7.95 (7H, m); 8–8.15 (2H, m).

m/*z* 196 (4), 195 (M − I, 29%), 106 (8), 105 (100), 89 (8), 78 (3), 77 (51).

2-Phenylbenzofuran (22).[32] Prepared following the procedure described elsewhere.[18] δ_H 7.04 (1H, s); 7.22–7.61 (7H, m); 7.87 (2H, m).

2-(2-Naphthyl)-1-phenylethanone (25).[33] Mp 117–118 °C. ν_{max}/cm^{-1}1689 (CO). δ_H 4.48 (2H, s, CH_2); 7.35–7.60 (6H, m); 7.70–7.85 (4H, m); 8.02–8.10 (2H, m). *m*/*z* 247 (1.4), 246 (M^+, 8.8%), 141 (11), 139 (5), 116 (1), 115 (17), 106 (7), 105 (100), 78 (2), 77 (35). Compared with an authentic sample prepared by photostimulated reaction of the anion of acetophenone with 2-iodonaphthalene in DMSO.

2-(1-Bromo-2-naphthyl)-1-phenylethanone (24). Solid. Found: M^+, 324.0137 and 326.0104. $C_{18}H_{13}BrO$ requires 324.0150. ν_{max}/cm^{-1} 1683 (CO). δ_H 4.71 (2H, s, CH_2); 7.35 (1H, d); 7.45–7.64 (6H, m); 7.77–7.85 (2H, m); 8.09 (2H, dd). *m*/*z* 246 (7.4), 245 (M − Br, 36.8%), 221 (2), 219 (3), 215 (3), 140 (16), 139 (24), 106 (7), 105 (100), 78 (4), 77 (44).

2-(2-Bromophenyl)-1-phenylpropanone (27b). Mp 49–50 °C. δ_H 1.48 (3H, d, CH_3); 5.11 (1H, q, CH); 7.1–7.6 (8H, m); 7.9 (1H, dd). δ_C 17.8 (Me), 47.0 (CH), 123.9 (C-Br), 128.1, 128.4, 128.5, 128.6, 132.9, 133.4 (q), 141.0 (q), 200.0 (CO). *m*/*z* 209 (M − Br, 7%); 106 (8); 105 (100), 78 (4); 77 (37).

1,2-Diphenylpropanone (28). Mp 40–41 °C (lit. 50–52 °C).[7a] δ_H 1.53 (3H, d, CH_3); 4.68 (1H, q, CH); 7.1–7.6 (9H, m); 7.9 (1H, dd). δ_C 19.5 (Me), 47.9 (CH), 126.9, 127.8, 128.5, 128.8, 128.9, 132.7 (c), 141.5 (c), 200.3 (CO). *m*/*z* 210 (M^+, 2%), 106 (8), 105 (100), 78 (4), 77 (33).

Acknowledgements

This work was supported by the Agencia Córdoba Ciencia, FONCYT, the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Fundación Antorchas and SECYT, Universidad Nacional de Córdoba, Argentina.

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