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Steady-state photochemistry (Pschorr cyclization) and nanosecond transient absorption spectroscopy of *twisted* 2-bromoaryl ketones*

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Abstract: The steady-state as well as transient absorption spectroscopy of a series of 2-bromoaryl ketones have been comprehensively examined to gain insights concerning (i) the transient phenomena (absorption spectral attributes as well as lifetimes), (ii) rates of C–Br homolysis, and (iii) the behavior of 2-aroylaryl radicals thus generated. The X-ray crystal structure analyses of selected ketones in which the mesomeric effects operate differently reveal that the two aryl rings are drastically *twisted* about the C=O bond. The twisting manifests itself in the spectral features of the transients, attributed to triplet–triplet (T–T) absorptions, such that they are not readily comparable in some cases to the transients of parent diaryl ketones that lack the 2-bromo group. By associating triplet decays with C–Br cleavage rates, the absolute rate data have been determined for diverse 2-bromoaryl ketones. With the exception of 2-bromo ketones containing *meta*-methoxy substituents, all other ketones are found to undergo efficient C–Br bond cleavage with rates of ca. 0.1–1.0 × 10^8 s^{-1}. For *m*-methoxy-substituted ketones, intriguingly slower deactivation of the triplets was observed. Based on solvent-dependent variation of the lifetimes (longer lifetimes in polar solvents), intramolecular charge transfer has been proposed. The preparative photochemistry and transient phenomena permit invaluable inferences as to the reactivity of 2-aroylaryl radicals in general. Quantum yield determinations and product analyses reveal that highly electrophilic aryl radicals undergo radical recombination, in a poor hydrogen-donating solvent, almost exclusively (>90 %) in the absence of incentive for stabilization via conversion to π-conjugated hydrofluorenyl radicals. Of course, when the latter is feasible, Pschorr cyclization leads to productive photochemical outcome. Moderately electrophilic radicals that lack stabilization via conversion to hydrofluorenyl radicals lend themselves to intramolecular 1,5-hydrogen shifts in conjunction with the formation of dehalogenated diaryl ketones and cyclized fluorenones (Fls) or its analogs.

Keywords: flash photolysis; homolysis; ketones; mesomeric effect; Pschorr cyclization; radical; triplet–triplet absorption.

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INTRODUCTION

Intramolecular homolytic substitution of arenes by aryl radicals, which are generated by decomposition of arene diazonium salts either thermally or photochemically or in the presence of Cu(I) salts, is called the Pschorr reaction [1]. The original Cu(I)-mediated decomposition of arenediazonium salts as well as its modified versions have been immensely exploited in organic synthesis [1h,i,2]. In general, the aryl radicals can be generated in a number of ways involving a range of mechanisms, and their generation and reactivity have been subjects of several investigations [3]. The acyl- or benzoyl-substituted aryl radicals, in particular, feature a unique category of aryl radicals [4]. Baum and Pitts showed for the first time that direct photolysis of halophenones, viz., iodo- and bromo-substituted benzophenones, leads to 2-benzoylphenyl radicals via C–X bond homolysis [5]. Subsequently, Wagner and co-workers delineated mechanistic aspects of C–X homolysis of all the regioisomers of iodo- and bromo-substituted acetophenones (APs) as well as benzophenones (BPs) [6]. The 2-benzoylaryl radicals, generated either by photoinduced homolysis of 2-iodobenzophenones or by Cu(I)-mediated decomposition of the precursor arenediazonium salts, have been scrutinized thoroughly for C–H migrations over the BP skeleton [7]. Surprisingly, the competitive intramolecular cyclization of such 2-aroylphenyl radicals to yield fluorenones (Fls) has not been explored in detail. Even the photochemistry of 2-haloketones is limited to simple BPs. In our recent studies, we showed that 2-benzoylphenyl radicals undergo cyclization to Fls in varying yields that are primarily determined by the nature of substituents and their location in the two aryl rings [8]. We have expanded these initial investigations to include 2-bromoheteroaryl ketones (Chart 1), and undertaken steady-state photochemistry as well as flash-photolysis investigations with the following objectives: (i) BPs have historically served as prototype examples to unravel the photoinduced reduction of carbonyl compounds in general and ketones in particular [9]. Despite the fact that the literature is replete with their photochemistry, investigations on the transient phenomena associated with 2-halobenzophenones are rather scarce, vide infra. The bulky halo group at the *ortho* position should be expected to cause steric inhibition of resonance leading to unique structural attributes that are intermediate between those of the true structures of BP and AP. Indeed, the bromophenyl ring is found to be considerably twisted from the remaining benzoyl moiety as revealed by recent X-ray structural determinations [10]. Thus, the transient phenomena associated with such ketones deemed fundamentally important. (ii) It has been shown by Wagner and co-workers that C–Br cleavage for *o*-bromoketones occurs from the triplet-excited state much faster than for *meta* and *para* analogs [6c]. The C–Br homolysis rate constants are presently known only for the parent *o*-bromobenzophenone via Stern–Volmer quenching kinetics, and the absolute rate data for the parent ketone [6c] as well as its derivatives are heretofore unknown. Thus, we wished to determine the rate data for a broad set of ketones in Chart 1. (iii) As mentioned earlier, the photochemically derived 2-aroylaryl radicals feature a unique category of radicals, which may undergo intramolecular aryl substitution to afford cyclic products in competition with hydrogen abstraction. Their reactivity should be expected to be governed by the nature as well as the location of the substituents in both rings, as they may modify the electronic complementarity between the radical-containing ring (XPh) and the ring that is attacked (Ph) [11]. Thus, the ketones in Chart 1 were anticipated a priori to yield comprehensive insights concerning Pschorr cyclization as well as competitive hydrogen abstraction from the solvents.

Herein, we report the results of a comprehensive investigation involving the synthesis of a broad set of 2-bromoketones **1–11**, X-ray structure determinations (**1b**,**c**,**2a**), steady-state photochemistry and nanosecond transient spectroscopy.

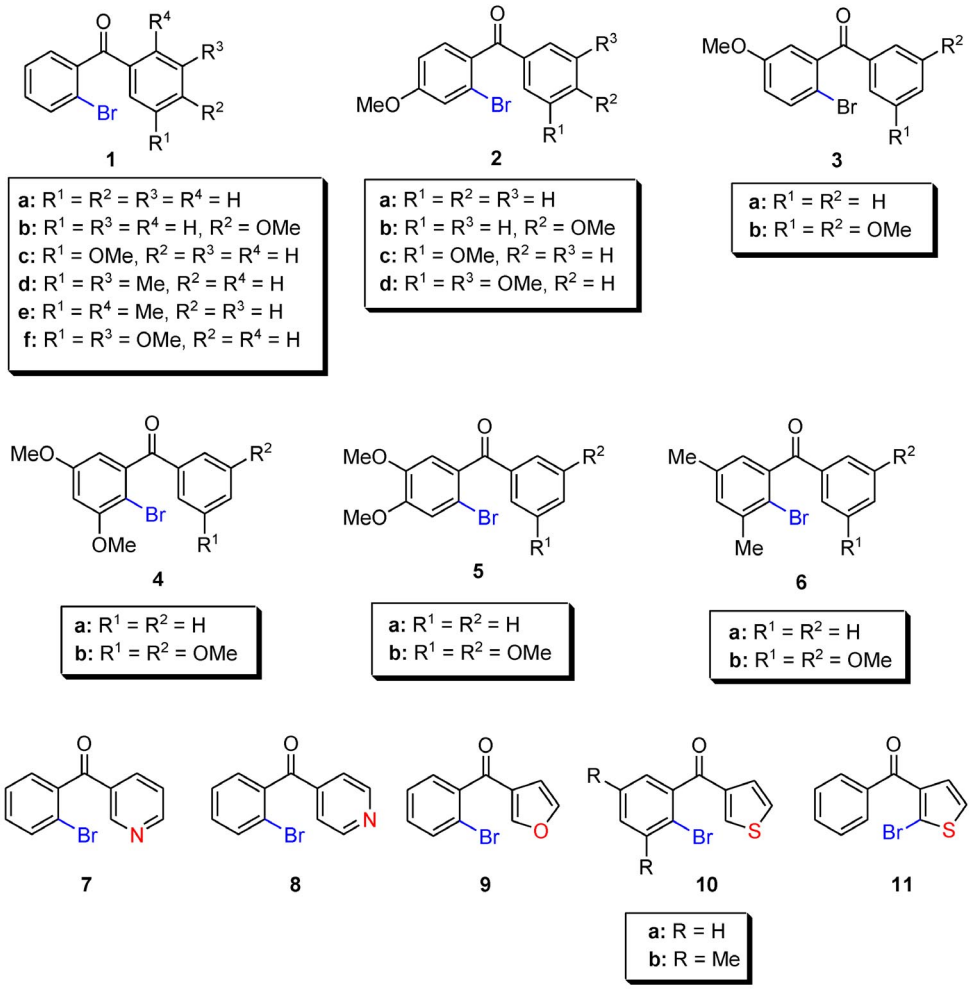


Chart 1. The structures of bromophenyl ketones (**1–11**) studied.

RESULTS

Synthesis of ketones

With the exception of **1e** and **3a**, the synthesis of all other ketones **1–6** as well as the results of their steady-state photochemistry have been reported by us previously [8]. The ketones **1e**, **3a**, **7**, **8**, and **10** were conveniently prepared by the reaction of 2-bromobenzaldehydes or appropriately substituted 2-bromobenzaldehydes with aryl magnesium bromides/heteroarylmagnesium chloride followed by pyridinium chlorochromate (PCC) oxidation of the resultant alcohols, cf. SI. Oxidation of the alcohol derived from the reaction of 2-bromophenylmagnesium chloride and 3-formylfuran using 2-iodoxybenzoic acid (IBX) afforded the ketone **9**. The reaction of 2-bromo-3-formylthiophene and phenylmagnesium bromide followed by PCC oxidation of the resulting alcohol led to ketone **11**, cf. SI.

Transient absorption spectroscopy of ketones 1–11

The transient phenomena of all ketones **1–11** were investigated by nanosecond flash photolysis (308 nm, excimer laser) of 2–20 × 10^{-4} M solutions of ketones **1–11** in nonpolar cyclohexane and car-

bon tetrachloride, and polar acetonitrile solvents. The flash photolysis of the parent 2-bromobenzophenone **1a** led to a transient, which is characterized by a strong band at ca. 320 nm followed by two minor bands at ca. 430 and 540 nm (Fig. 1). Whereas the ketone **8** was found to exhibit a similar feature, the longer wavelength band was found to disappear for **1b**. A comparison of the spectra for **1a**,**c**,**f** reveals a progressive blue-shift of the band at longer wavelength for the ketones containing *m*-methoxy substituent (Fig. 2). All other ketones **1b**,**d**,**e**,**3b** and the 2-halophenyl heteroaryl ketones **7–11** invariably exhibited a strong band at ca. 310–340 nm followed by absorptions in the region of 400–450 nm; the band at ca. 530 nm was observed for some cases and not for some others, see SI. For ketones **2a**,**b**,**3a**,**4–6**, the transient absorptions were too weak and short-lived (τ ca. 10–25 ns) to permit reliable spectral acquisition.

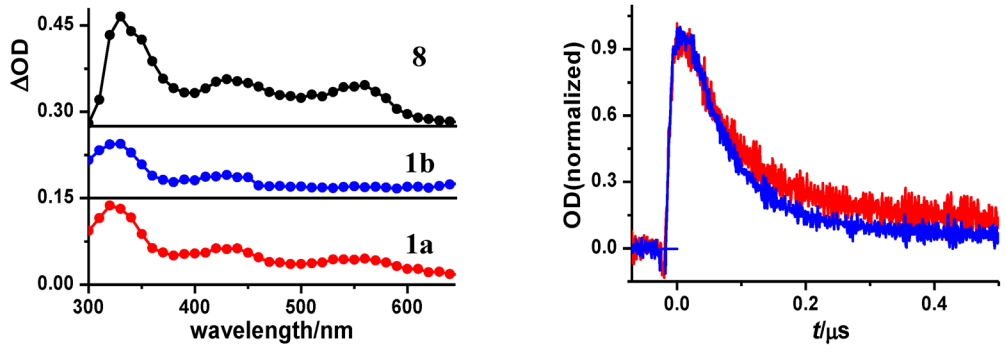


Fig. 1 The transient absorption spectra of **1a**,**b**,**8** in CCl_4, assigned to T–T transitions, recorded after 55 (**1a**,**1b**) and 34 ns (**8**) following nanosecond laser-flash photolysis (left). The normalized decay profiles for **1a** (blue) and **8** (red) in CCl_4 monitored at 450 nm (right).

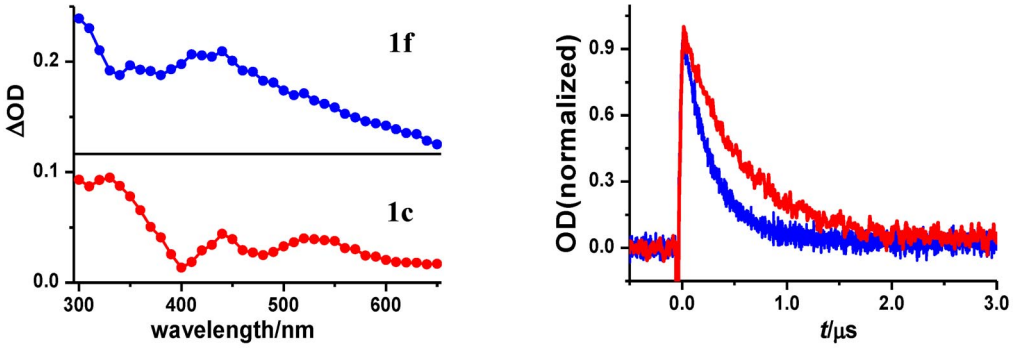


Fig. 2 The transient absorption spectra assigned to T–T absorption of ketones **1c**,**f** in CCl_4 after 75 (**1c**) and 150 ns (**1f**) following nanosecond laser-flash excitation (left). The normalized decay profiles for **1c**,**1f** monitored at 530 nm (right).

The transient absorptions in Figs. 1 and 2 for ketones **1a–c**,**1f**,**8** as well as for all other cases were assigned to their respective triplet–triplet (T–T) absorptions based on the following experimental results for **1a**,**c**, the representative cases. First, the transient absorption in each case was found to be quenched by molecular oxygen; the estimated rate constants for **1a**,**c** in CCl_4 respectively were 2.2 and 1.8 × 10^9 M^{-1} s^{-1}, well in the range expected for BPs. Second, the transients were found to be efficiently quenched by low-energy triplet quenchers such as 1,3-cyclohexadiene or 2,3-diazabicyclo[2.2.3]nonene

(DBN) with rate constants of (3.0 ± 0.5) × 10^9 M^{-1} s^{-1} for **1a**,**c** in cyclohexane and in CCl_4, cf. SI. Third, an excellent hydrogen donor such as 1,4-cyclohexadiene was found to ineffectively quench the transient absorption. The quenching rate constants of both **1a**,**c** with this donor were determined to be only ca. 4–9 × 10^6 M^{-1} s^{-1}. In particular, the rate constants determined for energy-transfer quenchers (O_2, cyclohexadiene, and DBN) eliminated the possibility of the transient absorption as being due to radicals.

In view of the relatively longer lifetimes for **1b**,**c**, cf. vide infra, the absorption spectra were examined for these ketones in three different solvents, i.e., cyclohexane, carbon tetrachloride, and acetonitrile. The transient absorption spectra that are attributable to T–T absorption are shown in Fig. 3, which suggest that for ketone **1c** in particular, the solvent-induced changes are significant. They reveal the fact that the absorption at ca. 540 nm is completely absent for **1b**, while the long-wavelength absorption bands of **1c** shift hypsochromically on going from cyclohexane to acetonitrile. For the sake of consistent comparison, the T–T absorption spectra were also recorded for AP, 3-methoxyacetophenone (3-OMeAP), 4-methoxyacetophenone (4-OMeAP), BP, 3-methoxybenzophenone (**1c**-BP), and 4-methoxybenzophenone (**1b**-BP) in CCl_4 as a solvent (Fig. 4). The strong absorption band at ca. 320 nm is uniformly present for the T–T spectra of all ketones, while the 450-nm band is observed only for APs and the 540-nm band for BPs.

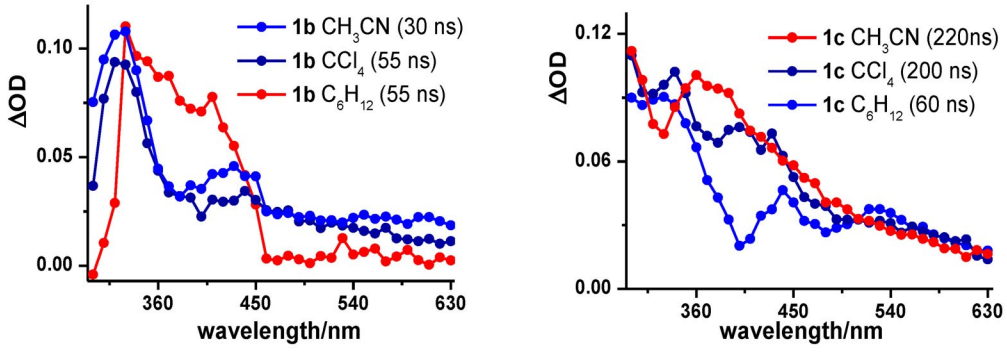


Fig. 3 The T–T absorption spectra of **1b** (left) and **1c** (right) in cyclohexane, carbon tetrachloride, and acetonitrile. Delay time for the spectral acquisition in each case is given in parentheses.

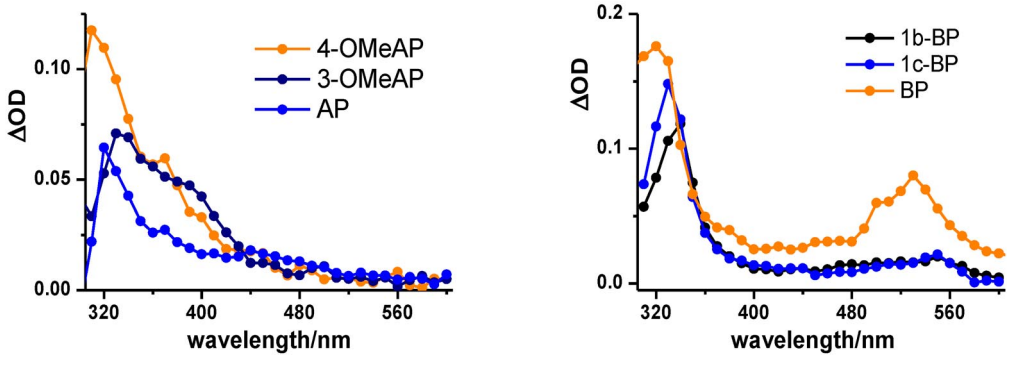


Fig. 4 The T–T absorption spectra of i) left: AP, 3-OMeAP and 4-OMeAP in CCl_4 recorded after 30, 550 and 750 ns following nanosecond laser flash excitation, and ii) right: BP, **1c**-BP and **1b**-BP after 750, 380, and 220 ns following excitation. Delay time for the spectral acquisition in each case is given in parentheses.

The transient absorptions thus assigned to the triplets were kinetically followed for all cases uniformly at 420–460 nm, as a small residual absorption in some cases interfered with the decays at 310–330 nm. Figures 1 and 2 show typical decay profiles recorded for ketones **1a**,**c**,**f**,**8**. The triplet lifetimes and decay rate constants ($1/\tau$, in CCl_4) determined for all ketones **1–11** in cyclohexane, carbon tetrachloride, and acetonitrile are collected in Table 1. A definite trend in the lifetimes is noteworthy. With the exception of *m*-methoxy-substituted ketones, i.e., **1c**,**f**,**3b**,**6b** (entries 3, 6, 12, and 18), all other ketones exhibit short lifetimes (<10 to 90 ns), and show solvent dependence in that they are uniformly shorter in acetonitrile than in nonpolar cyclohexane and carbon tetrachloride. Further, the lifetimes in CCl_4 are shorter than or equal to those in cyclohexane. For the *m*-methoxy-substituted ketones, the lifetimes are also significantly longer in addition to the fact that the solvent effect is opposite. While the lifetimes are found to vary from 275 ns in cyclohexane to 1000 ns in acetonitrile for **1c**, the additional *m*-methoxy-substitution raises the lifetimes much further from 650 ns in cyclohexane to 1700 ns in acetonitrile. It is the *meta*-disubstitution of a methoxy group that renders even the observation of triplets for some ketones that are otherwise not observable, e.g., compare **3a** vs. **3b** and **6a** vs. **6b**. For ketones **2a**,**b**,**3a**,**4a**,**b**,**5a**,**b**, the triplet lifetimes are very short (<25 ns). Interestingly, all the heteroaryl ketones **7–11** display measurable lifetimes with trends that are akin to **1a** (entries 19–23, Table 1).

Table 1 Lifetimes and decay rate constants of triplet-excited ketones in nonpolar (C_6H_{12} and CCl_4) and polar (CH_3CN) solvents.[a]

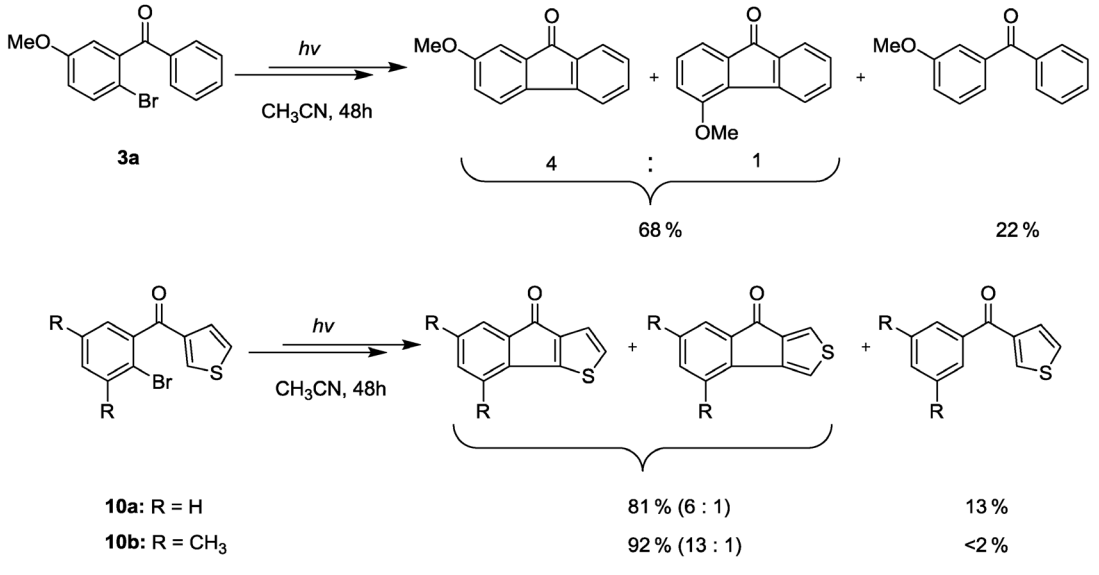
Entry	Ketone	Lifetimes (ns)[b]			$k(CCl_4)$	Benzene–Br•
		CCl_4	C_6H_{12}	CH_3CN	($\times 10^8$ s^{-1})	complex
1	**1a**	50	70	18	0.20	yes
2	**1b**	50	91	30	0.20	yes
3	**1c**	450	275	1000	0.02	yes
4	**1d**	90	85	35	0.11	weak
5	**1e**	90	115	43	0.11	weak
6	**1f**	1000	650	1700	0.01	no
7	**2a**	15	25	–[c]	0.66	yes
8	**2b**	10	–[c]	–[c]	1.00	yes
9	**2c**	60	45	80	0.17	yes
10	**2d**	150	90	260	0.07	weak
11	**3a**	20	20	17	0.50	weak
12	**3b**	77	67	85	0.13	no
13	**4a**	13	–[c]	–[c]	0.78	no
14	**4b**	13	–[c]	<10	0.78	no
15	**5a**	25	30	13	0.40	no
16	**5b**	20	26	<10	0.50	no
17	**6a**	17	17	–[c]	0.59	yes
18	**6b**	71	44	167	0.14	no
19	**7**	64	67	26	0.16	yes
20	**8**	45	40	26	0.22	yes
21	**9**	33	65	27	0.33	yes
22	**10**	70	70	74	0.14	yes
23	**11**	40	45	35	0.25	no

[a]Based on the decay kinetics of transient absorptions at their absorption maxima. The transients were produced by nanosecond flash photolysis (308 nm). Error ± 10 %.
[b]The decays in some cases were associated with high residual absorptions when monitored particularly at 310–330 nm.
[c]The signals were too weak and short lived to be monitored.

The photolysis of **1a** in benzene solvent led to a strong transient absorption with a maximum at 530 nm, cf. SI. The absorption is characteristic of the complex of bromine atom with benzene [12]. Indeed, 2-iodobenzophenone has likewise been reported to produce the complex of iodine and benzene with an absorption maximum at 490 nm [6b]. In a similar vein, such a benzene–Br$^{\bullet}$ complex formation has been reported to be observed upon photolysis of all bromo-substituted APs [6c]. We carefully examined each ketone to establish whether or not photolysis in benzene leads to the observation of benzene–Br$^{\bullet}$. The results of these observations are recorded in Table 1. The formation of the complex is indicative of C–Br cleavage. Further, whether or not the C–Br cleavage occurs in each case from triplet-excited state was probed by carrying out photolysis in the presence of a triplet quencher. At a concentration of 1,3-cyclohexadiene that is sufficiently high to quench the triplets completely (0.17 M), it was established that the photolysis of parent *o*-bromobenzophenone **1a** does not lead to benzene–Br$^{\bullet}$ complex. It is unlikely that the bromine atoms escape without being captured through competitive hydrogen atom abstraction from cyclohexadiene, which must lead to readily recognizable absorption due to cyclohexadienyl radical [13]. The fact that the latter is not observed suggests that C–Br cleavage occurs primarily from the triplet-excited state.

Steady-state photolysis and determination of quantum yields

As mentioned earlier, the results of photolyses for all ketones **1–6** with the exception of **3a** have been reported by us previously (Table 2) [8]. In the present investigation, the photochemistry of **3a** and heteroaryl analogs **7–11** was examined by subjecting their solutions to irradiation at 350 nm in a photoreactor. The photolysis of ketone **3a** for 48 h led to 57 % conversion of the ketone and yielded a regioisomeric mixture of two cyclized Fls in 68 % and the dehalogenated BP in 22 % isolated yields (Scheme 1). The yields of cyclization products from **7–9** were found to be poor (13–32 %, Table 2). For these cases, the results of photolysis were analyzed by gas chromatography (GC). The photolysis of ketones **10a**,**b** led to the corresponding mixture of cyclization products in 81 and 92 % isolated yields together with 13 and <2% yields of the dehalogenated ketones, respectively (Scheme 1). Notice that the structure of the minor cyclization product is unique. Ketone **11** was found to be highly unreactive even after irradiation for 48 h.



Scheme 1

We have determined the quantum yields for a few representative ketones with valerophenone actinometry. Accordingly, the solutions of ketones (ca. 0.04 M) were photolyzed with a monochromatic light (313 nm) from a high-pressure Hg-lamp, and the photolysates were analyzed by GC with methyl benzoate as an internal standard. Photodecomposition of valerophenone at 313 nm, which leads to the formation of AP with $\Phi = 0.33$, was employed as a chemical actinometer [14]. The conversions were limited to 6–15 %. The quantum yields thus determined for **1a–d**,**2a**,**b**,**6a** are given in Table 2. The cyclization and dehalogenation products, i.e., Fls and BPs, make up largely the products of ketone disappearance. Further, the quantum yields for disappearance of the ketones (Φ_d) are lowest (0.017) and highest (0.09) for the dimethyl-substituted ketones **6a** and **1d**, while they are 0.04–0.07 for all the methoxy-substituted ketones. In a similar manner, one observes more selective partitioning of the ketone disappearance between the only observable products, i.e., cyclized Fl and dehalogenated ketone, for ketones **1c**,**d**,**6a**, which is also reflected in the yields of isolated products from preparative-scale photolyses.

Table 2 Results of photolysis[a] and quantum yield determinations[b] of selected ketones.

Ketone	Fl (%)	BP (%)	Φ_d(ketone)	Φ(Fl)	Φ(BP)
1a[c]	34	62	0.050	0.020	0.022
1b[c]	48	39	0.070	0.033	0.032
1c[c]	75	20	0.050	0.040	0.010
1d[c]	67	21	0.090	0.065	0.020
2a[c]	48	39	0.050	0.024	0.021
2b[c]	48	34	0.040	0.025	0.015
3a	68[d]	22			
3b[c]	95	–			
4a[c]	–[e]	–[e]			
4b[c]	94[f]	–			
5a[c]	–[e]	–[e]			
5b[c]	75[g]	–			
6a[c]	80	–	0.017	0.013	0.002
7[h]	13	62			
8[h]	22	46			
9[h]	32	11			
10a	81[i]	13			
10b	92[i]	<2			
11	–[e]	–			

[a]From preparative photolysis, ca. 100–150 mg (0.5–0.6 mmol) of the haloketone was subjected to photolysis at 350 nm. Unless otherwise mentioned, the yields refer to isolated yields from preparative-scale photolysis.
[b]The quantum yields were determined for irradiation at 313 nm and from quantitative GC analysis using valerophenone actinometry. Error ± 10 %.
[c]From [8].
[d]A mixture of regioisomeric products, conv. 57 %, see text.
[e]<7–8 % Conversion even after 48 h of irradiation.
[f]Conv. 58 %.
[g]Conv. 76 %.
[h]From GC analyses.
[i]A mixture of regioisomeric products, see text.

X-ray structure determinations of ketones 1b,c,2a

To gain more insights concerning the molecular structures of *o*-halobenzophenones, we undertook structural investigations of some of the ketones. In particular, we determined the structures of **1b**,**c**,**2a** to gauge the influence of the methoxy group when located in the two rings and at different locations; in particular, the structures of **1b**,**c** were anticipated to reflect the influence of mesomeric effect and lack of it in the two structures.

The crystals of **1b**,**c**,**2a** were readily grown by slow evaporation of their solutions in a combination of solvents involving EtOAc/$CHCl_3$/CH_2Cl_2 and pet. ether. The intensity data were collected by a charge coupled device (CCD) single-crystal diffractometer and were processed with SHELX software, cf. Supplementary Information. The perspective drawings of the molecular structures of all ketones **1a–c**,**2a** are shown in Fig. 5; the crystal structure of 2-bromobenzophenone **1a** has previously been reported [15]. As may be readily seen, the two aryl rings in the structures of all ketones are twisted with respect to the C=O group. The torsion angles involving O1,C13,C1,C2 (ψ_1) and O1,C13,C7,C8 (ψ_2) atoms may be considered to reflect the twisting of bromophenyl ring and the other aryl ring with respect to the carbonyl functionality. In a similar manner, the mutual twisting of the two aryl rings, i.e., the angle between the planes θ, may also be considered. The torsion angles (ψ_1 and ψ_2) and the angle between the planes of the aryl rings (θ) thus calculated for BP and its bromo derivatives **1a–c**,**2a** are collected in Table 3. Whereas the values of ψ_2 fall in the range of ca. 150–167º, those of ψ_1 lie between 100–135º, which clearly suggests that the bromophenyl ring twists considerably with respect to the C=O group, while the other aryl ring tends to be conjugated. The effect of methoxy substituent when located at the *para* position to the carbonyl in the bromophenyl ring and the other aryl ring is quite instructive. The torsion angle data in Table 3 show that the resonance involving the methoxy group with that of the carbonyl functionality reduces the twisting of that phenyl ring which contains the methoxy substituent at para position. As a consequence, the Br-phenyl ring becomes much more twisted in **1b** (ψ_1 = 100.29º vs. 106.46º for **1a**), while it is significantly reduced in the case of **2a** (ψ_1 = 121.48º vs.

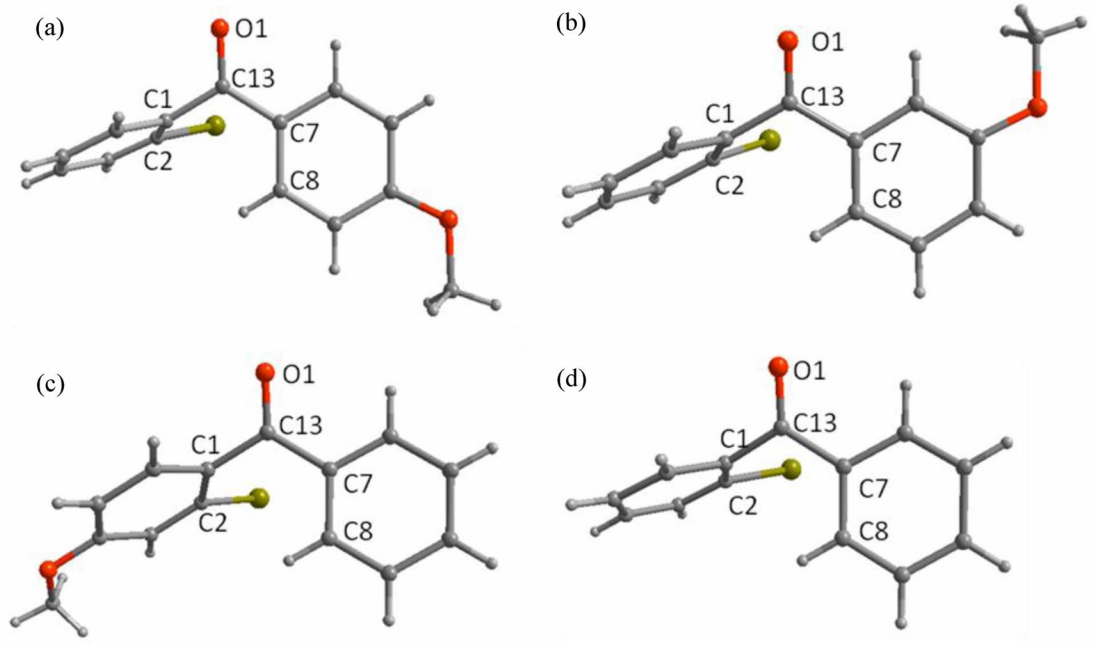


Fig. 5 The X-ray-determined molecular structures of **1b** (a), **1c** (b), **2a** (c), and the parent 2-bromobenzophenone **1a** (d); the structure of **1a** is literature-reported, and was generated by its coordinates (refcode: PAMWOQ).

106.46º for **1a**). Further, a comparison of the values of θ reveals that the *m*-methoxy group in **1c** contributes to diminishing the noncoplanarity of the bromophenyl ring in **1c** relative to that in **1a**. While the crystal packing forces might influence the conformations, it is more often than not that the molecules crystallize in their lowest-energy conformations [16]. Thus, the knowledge of conformational preferences as available from solid-state molecular structures should be expected to be of direct relevance to their photochemistry.

Table 3 The calculated torsion angles (ψ_1 and ψ_2) and the angle between the planes of the aryl rings (θ) for the X-ray-determined structures of **BP**, **1a–c**,**2a**.

Compound	Torsion angle (º)		Angle between the planes θ (º)
	ψ_1	ψ_2	
BP[a]	135.12	149.95	64.61
1a[b]	106.46	161.22	80.32
1b	100.29	167.49	85.78
1c	114.14	159.21	78.95
2a	121.48	157.72	75.05

[a]**BP** = benzophenone.
[b]Ref. [15].

DISCUSSION

Following initial findings by Baum and Pitts that bromo-substituted ketones undergo photoinduced C–Br bond cleavage [5], Wagner and co-workers comprehensively investigated the mechanism of C–Br cleavage in 2-bromobenzophenones [6a,c]. They showed that *o*-, *m*-, and *p*-bromoacetophenones undergo photoinduced cleavage to yield bromine radicals. While *m*- and *p*-bromobenozphenones were found to cleave inefficiently, *o*-bromobenzophenone was shown to be 500 times more reactive [6c]. Based on a combination of steady-state and laser flash studies, Wagner et al. concluded that the C–Br homolysis occurs, despite the endothermicity associated with C–Br cleavage as a consequence of low triplet excitation energy (ca. 69 kcal/mol for BPs and 72–74 kcal/mol for APs) [6a,c,9a], via thermally activated conversion of a π,π^* triplet into a dissociative $n_{Br}{}^{\pi},\sigma^*$ state with the mixing of $n_{Br}{}^{\pi},\pi^*$ character into π,π^* state providing the requisite coupling between electronic states [6c]. In both bromo-substituted AP and BPs, the n,π^* states are assumed to convert into π,π^* triplets before cleavage (Fig. 6). The high reactivity of *o*-bromobenzophenones has been ascribed to steric lowering of C–Br bond dissociation energy.

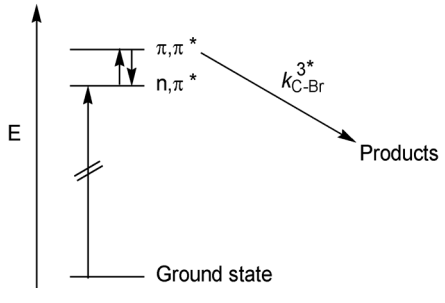


Fig. 6 The electronic states responsible for photoinduced C–Br homolysis of 2-bromobenzophenones.

For all 2-bromoketones **1–8** in which the two aryl rings are 6-membered, sterically accelerated C–Br cleavage may prevail, while such a consideration should be different for ketones **9–11** that contain 5-membered heterocyclic rings. The fact that the latter also undergo rapid C–Br homolysis is reflected in the rapid deactivation of their triplets as well as associated preparative photochemistry (Tables 1 and 2). In the following, we shall first consider the spectral attributes of 2-bromoketones followed by rate constants for C–Br homolysis and mechanistic aspects of how the substituents influence Pschorr cyclization in particular and the overall photochemical outcome of 2-halobenzophenones in general.

Influence of *o*-bromo substitution on the absorptions of ground and triplet-excited states of ketones

A perusal of the absorption spectra of APs, BPs, and the corresponding 2-bromo analogs (cf. SI) reveals a perceptible difference in the absorption features of **1b** and **2a**, which contain a *p*-methoxy group in Ph and BrPh rings, respectively. While the absorption of **2a** is rather similar to that of **1a**, **1b** shows different features. In a similar manner, the *m*-methoxy substituent in Ph and BrPh rings as in **1c**,**3a** produces differences in their absorption spectra, cf. SI. Clearly, the substituents produce varying degrees of influence on the absorption spectra depending on which of the two phenyl rings of 2-bromobenzophenone nucleus that they are part of. The fact that such effects also manifest in the absorptions of the transient intermediates, assigned to T–T absorptions, is evident from Figs. 1 and 2. The T–T absorption of **1a** in cyclohexane/carbon tetrachloride is characterized by a strong band at 320 nm followed by two bands of moderate absorption at ca. 450 and 550 nm. A similar 3-band feature is observed for the triplets of **1c**,**d**,**2c**,**7**,**8** (Figs. 1 and 2, and SI). While the long-wavelength absorption is found to be absent for the triplet of **1b**, the *m*-methoxy ketones **1c**,**f** are found to exhibit broad and strong absorptions in the long wavelength region between 400–600 nm (Fig. 2). From a comparison of the T–T absorptions of *o*-bromoketones with a variety of BPs that are devoid of *o*-bromo groups (Fig. 4), the 320- and 550-nm bands can be readily associated with the BP chromophore. What is otherwise intriguing is the origin of the 450-nm band and the absence of the 550-nm band in ketones such as **1b**.

To understand the chromophores that are responsible for the observed spectral characteristics, let us consider the structural changes that are attendant upon substitution of BP with various groups. The two phenyl rings in parent BP are twisted (θ = 64.6º, Table 3) [15]. The *o*-bromo substituent in **1a** further increases the nonbonding steric interactions such that the aryl rings are further twisted (80.3º). Relative to **1a**, the twisting angle θ differs considerably for the methoxy-substituted 2-bromobenzophenones, viz., **1b**,**c**,**2a**. While the value of θ is as high as 85.8º for **1b**, it is 75.0º for **2a**; for **1c**, it is intermediate between the two, and closer to what it is for **1a**. These observed differences in the values of θ for **1b** and **2a** relative to **1a** may be reconciled based on mesomeric effects. The resonance due to delocalization of the lone pair of 4-methoxy group in **1b** should cause the *p*-methoxyphenyl ring to become more coplanar with respect to the CO group such that the BrPh ring twists more relative to the parent ketone **1a**. In a similar manner, the resonance due to 4-methoxy group in **2a** should lead to more coplanarization of the BrPh ring with respect to the C=O group such that the twisting is reduced. Thus, the dihedral angles ψ_1 and ψ_2 as well as the angles between the planes of aryl rings in Table 3, revealed by the solid-state structures, are in complete accord with the expectations based on resonance effects. Insofar as the solution state is concerned, the low-energy geometries as revealed by the X-ray determined structures are likely to contribute predominantly, among various possible conformations, to the description of overall molecular structure. Based on this premise, the ketone **1b** with near orthogonality between the aryl rings should be expected to exhibit ground- and excited-state absorption properties that mimic *p*-methoxyacetophenone. The complete absence of the 550-nm band in the case of **1b**, which is typical of BP triplet, is clearly suggestive of this scenario. The band at 450 nm is presumably a result of the influence of 2-bromophenyl ring on the absorption of *p*-methoxybenzoyl chromophore, which is otherwise found as a shoulder at ca. 390 nm in *p*-methoxyacetophenone (Fig. 4). For **1a** with compar-

atively lesser orthogonality, the appearance of both 450- and 550-nm bands should be reconciled from different proportions of equilibrating conformations that correspond to AP as well as BP chromophores. This rationalization follows from the notion that changes in the triplet absorptions—despite the fact that the excited states are electronic isomers—can be correlated with ground-state chromophores, just as the changes in the absorption spectra can be correlated.

The *meta*-methoxy substitution of 2-bromoketones evidently changes both ground-state and T–T absorption spectral features. 3-OMeAP, 1c-BP, **1c**, **1f**, and **3a** show long wavelength absorption bands that are associated with high molar absorptivities unlike those of *para*-analogs (**1b** and **2a**), cf. SI. It is known that 3-methoxy substitiution of **AP** stabilizes π,π* relative to n,π* state such that the lowest excited triplet is π,π* [9a,17]. A comparison of the absorption spectra of 1c-BP vs. 3,5-dimethoxybenzophenone and 2-bromoketones **1c** vs. **1f** reveals red-shifted absorptions, which point to the fact that additional substitution brings about increased stabilization. The T–T absorption spectra in Fig. 2 as well as the dihedral angles ψ_1 and ψ_2 together with angle between the planes (θ) in Table 3 point to equilibrating conformations that reflect the signatures of both AP- and BP-like chromophores [18].

The T–T absorption spectra of pyridyl ketones **7** and **8** exhibit a 3-band feature similar to **1a** (Fig. 1), while **9** and **10a** display notable differences [19]. The ketone **11** shows a 2-band pattern similar to BP.

Absolute rate constants for C–Br homolysis

The lifetime data in Table 1 show that all bromoketones with the exception of those that contain methoxy group/s in the meta postion/s of the Ph rings, i.e., **1c**,**f**,**2d**, exhibit lifetimes that vary within 10–90 ns in a solvent such as CCl_4. The lifetimes in cyclohexane and acetonitrile follow similar trends for those ketones that lack *m*-methoxy groups; notably, the lifetimes are lower in acetonitrile relative to those in CCl_4 or cyclohexane. For *m*-methoxyketones such as **1c**, the lifetimes increase on going from cyclohexane to CCl_4 to acetonitrile. Photolysis in a solvent such as benzene is quite instructive to probe the cleavage and formation of Br radicals. Except for the *meta*-methoxy substituted ketones **1f**,**3b**,**4,5**,**6b** and bromothienyl phenyl ketone **11**, the fact that the flash photolysis of all other ketones leads to C–Br homolysis was established by the diagnostic absorption of benzene–$Br^{\bullet}$ complex, which exhibits a distinct and strong absorption with a maximum at 490 nm, cf. SI.

The high triplet decay rate constants determined earlier for the parent 2-bromobenzophenone **1a** as well as its *meta* and *para* isomers by Wagner and co-workers via Stern–Volmer kinetics of thiol quenching have been assigned to direct bond cleavage, i.e., $k_{C–Br}$ [6c]; they have argued that the contributions of phosphorescence and radiationless mechanisms via spin-orbit coupling induced by the heavy Br atom substituent to the overall triplet decay cannot be significant in light of their high decay rate constants that are in the order of 10^8 s^{-1} [6c]. Thus, the triplet decay rate constants, i.e., $1/\tau$, in Table 1 should be directly attributed to C–Br bond cleavage, i.e., $k_{C–Br}$. The estimated rate constant for C–Br cleavage, i.e., $k_{C–Br}$, for the parent 2-bromobenzophenone in benzene solvent based on thiol quenching Stern–Volmer kinetics was found to be 0.7×10^8 s^{-1} [6c]. A perusal of the results in Table 1, which are derived from measurement of triplet lifetimes, shows that the values determined in CCl_4, cyclohexane, and acetonitrile vary in the range of $0.05–0.20 \times 10^8$ s^{-1} (Table 1). Let us consider the triplet decay rates in CCl_4 in which the T–T absorptions could be monitored for all ketones. As given in Table 1, a variety of substituted ketones, with the exception of *m*-methoxy substituted ketones **1c**,**f**,**2d**,**6b**, exhibit high triplet-state C–Br cleavage rate constants. For ketones **3b**,**4**,**5**,**6b**,**11**, the high triplet decay rate constants ($k_{C–Br}$ (CCl_4) ca. $0.14–0.5 \times 10^8$ s^{-1}) attest to the fact that the C–Br cleavage does occur for these cases as well. The fact that the $Br^{\bullet}$ is not observed is due presumably to rapid recombination or as a result of the concentration of Br radicals that escape from the solvent cage of the initially formed geminate radical pair being too low as to be detectable. The recombination of radical pairs within the solvent is seemingly very efficient.

We believe that the observed rate differences are a manifestation of small differences in the energies of the lowest n,π* and the next higher π,π* triplet states. As noted earlier, Wagner et al. have argued that the C–Br cleavage in Br-BPs must occur via conversion of the lowest n,π* states into π,π* states (Fig. 6). Otherwise, it is instructive to recognize that substitution in the BrPh ring vis-à-vis Ph ring leads to a dramatic rate differences.

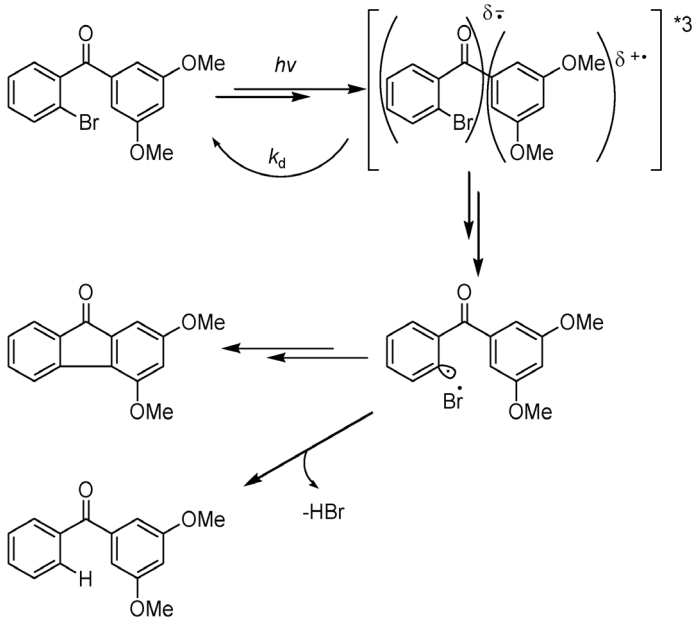
Intramolecular charge transfer in *m*-methoxy-substituted ketones

What is noticeable from the lifetime/rate data in Table 1 is that the ketones **1c** and **1f** that contain methoxy groups at 3 and/or 5 positions exhibit significantly longer lifetimes as compared to that of **1a**. Indeed, the 3,5-dimethyl substitution also increases the lifetime moderately. A similar, albeit less pronounced, effect is also observed for 2-bromo-4-methoxybenzophenones.

Strikingly different photobehaviour of phenyl ketones when substituted with *m*-methyl/acetoxy/methoxy susbstituents as compared to those of the *para* isomers has long been recognized [17]. Insofar as the photochemistry of alkyl phenyl ketones such as butyrophenone and valerophenone are concerned, the triplets are known to decay with low quantum yields of decomposition as compared to their *para*-substituted analogs; indeed, the *m*-methoxy groups are known to lower the reactivity by two orders of magnitude [17]. These anomalous observations have been reasoned based on the consideration that the *m*-methoxy substituent stabilizes π,π* states relative to those of the n,π* states via charge-transfer mechanisms. The UV–vis absorption spectra of substituted APs, BPs, and 2-bromobenzophenones clearly reflect these trends, cf. SI. Indeed, the triplet excitation energies of *m*- and *p*-methoxybenzophenones determined from phosphorescence spectra reveal a significant lowering by ca. 0.6–1.0 kcal mol^{-1} [20]. Thus, in light of the fact that the lowest n,π* triplet states of bromobenzophenones are intrinsically non-dissociative and that the cleavage, as mentioned above, is argued to occur via the upper π,π* state (Fig. 6), the reduction in the excitation energy should manifest in increased difficulty of C–Br cleavage. Thus, the slow triplet decay of the *m*-methoxy-substituted ketones should be reconciled based on the lowering of the triplet excitation energy via stabilization of the π,π* state. It is interesting to note that the stabilization of the π,π* state is apparently more for ketones substituted with the *m*-methoxy groups in the Ph ring as opposed to BrPh rings as reflected from their triplet lifetimes (entries 2, 3, 6, 7, 11, and 13, Table 1).

It is evident from Table 1 that the triplet lifetimes of ketones **1c**,**f**,**2d** are highly solvent-dependent. While the lifetimes are comparable in CCl_4 and cyclohexane, they increase considerably in polar solvents such as acetonitrile. This is in stark contrast to the behavior of all other ketones (Table 1). The increase in lifetimes in polar solvents should be a result of the stabilization of charge-transfer states. As shown in Scheme 2, deactivation of charge-transfer complex in a nonproductive way (k_d) may also contribute to the overall triplet decay such that the triplet decay rates for these cases do not represent true C–Br cleavage rate constants. However, the endothermicity for C–Br cleavage might partially be offset by partial charge transfer [17,20,21], which may abet the C–Br cleavage (Scheme 2).

For ketones containing e-donating substituents such as methyl or methoxy at *meta* position/s, intramolecular charge transfer effects may interfere to modify the triplet decay rate constants, as observed for ketones **1c**,**f**,**2d**,**3b**,**6b**. For all these cases, the triplet decay may not necessarily be determined by C–Br bond cleavage. It is well known that partial charge transfer complexes deactivate unproductively to the precursor reactants [20]. Thus, the rate constants for triplet decays in these cases are unlikely to represent C–Br cleavage rates. Otherwise, the excellent preparative photochemistry that leads to predominant Pschorr cyclization products should be assisted by the charge-transfer pathway (Scheme 2).



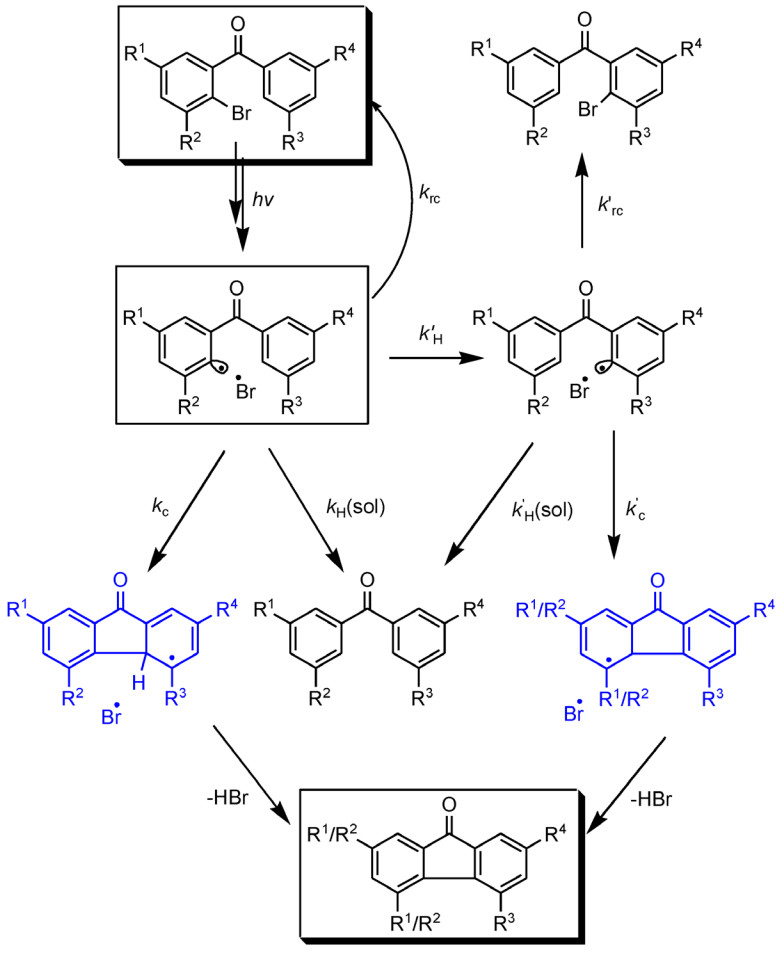
Scheme 2

Mechanistic rationalizations concerning hydrogen abstraction and Pschorr cyclization of 2-aroylphenyl radicals

The fact that the reactivity of *o*-bromobenzophenones is entirely triplet-derived has long been established [6a,c]. As reasoned earlier, the high triplet decay rate constants for all ketones that do not contain e-donating substituents at the *meta* position/s imply that the C–Br bond cleavage is primarily responsible for the triplet deactivation. Thus, the photolysis of 2-bromophenones lacking e-donating substituents at *meta* position/s may in principle lead to 2-aroyl radicals with close to unit efficiency. The partitioning of 2-aroylradicals between radical recombination (k_{rc}), hydrogen abstraction from the solvent (k_H(sol)), intramolecular hydrogen abstraction (k'_H) to yield translocated radical and intramolecular attack to yield hydrofluorenyl radical (k_c), as shown in Scheme 3, determines the overall photochemical outcome and efficiency.

In our ns-transient absorption spectroscopy, we did not observe growth of any transient in conjunction with the disappearance of T–T absorption for all the ketones examined. Further, the T–T absorption decay profiles were found to be monoexponential [21], suggesting thereby that most aryl radicals that are formed initially as radical pairs collapse back to regenerate ketones. Indeed, the quantum yields of ketone decomposition typically determined for some of the ketones (Table 2) suggest that the radical recombination, i.e., k_{rc}, is the predominant pathway occurring with >90–98 % efficiency. Otherwise, the competition between hydrogen abstraction and intramolecular attack, which lead to dehalogenated BP and cyclized Fl, respectively, determine the photoproduct distributions.

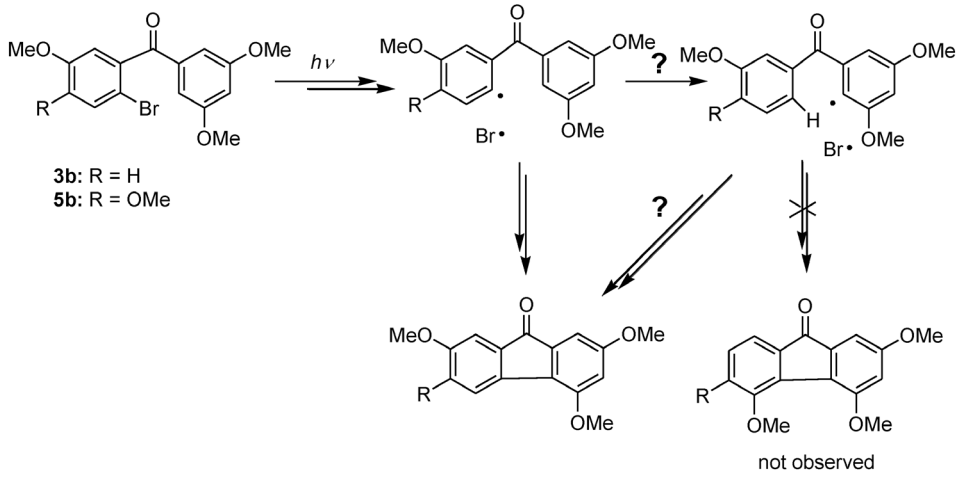
The translocated aroylaryl radical generated via intramolecular 1,5-hydrogen abstraction of the initially formed radical (k'_H) may collapse to a rearranged bromoketone (k'_{rc}), dehalogenated BP (k'_H(sol)) and cyclized Fls (k'_c) (Scheme 3). Unless the ketones are appropriately functionalized, the reactivity via 1,5-hydrogen shift cannot be readily perceived. Through isotope labeling, Karady et al. have shown that the radical translocations do occur for the parent 2-benzoylphenyl radicals [7a,b]. Further, they have also shown that photolysis of 4'-bromo-2-iodo-5-methylbenzophenone lends itself to the recognition of such intramolecular 1,5-hydrogen shifts through cyclization as well as aromatic substitution products, when the photolysis is carried out in aromatic solvents [7a]. Of all the ketones **1–11**



k_{rc} favored: $R^1 = R^2 = OMe$, $R^3 = R^4 = H$
k_c favored: $R^3 = R^4 = OMe$
k'_c favored: $R^1 = OMe$, $R^2 = R^3 = R^4 = H$
k_H favored: $R^1 = R^2 = H$, $R^3 = R^4 = H/Me$

Scheme 3

of the present investigation, only **3a**,**b**,**5a**,**b** may lend themselves to the recognition, through the formation of cyclization products, of the occurrence of 1,5-hydrogen shifts in the photochemically derived 2-aroylphenyl radicals. We have found that the ketones **3b** and **5b** yield Fls via the initially formed aroylphenyl radicals with no evidence whatsoever for the reactivity from the translocated radical. In other words, the regioisomeric Fls resulting from the translocated radicals were not observed from both **3b** and **5b** (Scheme 4). The ketone **5a** was found to be virtually unreactive, while **3a** yielded isomeric cyclization products as shown in Scheme 1, suggesting the occurrence of radical translocations. The photobehavior of this set of ketones, i.e., **3a**,**b**,**5a**,**b**, is sufficiently suggestive of the reactivity of 2-aroylphenyl radicals in general, and also offers crucial insights concerning their reactivity.



Scheme 4

The fact that photolytically generated initial 2-aroylaryl σ-radicals [23,11b] preferably undergo cyclization, under conditions involving the use of a solvent such as acetonitrile that suppress intermolecular hydrogen abstractions (k_H(sol)), when their hydrofluorenyl π-radicals are stabilized is suggested by the reactivity of **3b** and **5b**; these ketones undergo cyclization to afford Fls in excellent isolated yields. That the 2-aroylaryl σ-radicals explore intramolecular hydrogen abstractions (1,5-hydrogen shift) in the absence of such a stabilization via conversion to hydrofluorenyl π-radicals is revealed by the reactivity of ketone **3a**, which permits occurrence of translocation to be recognized in the cyclized Fls (Scheme 1). The lack of photoreactivity of **5a** in conjunction with very short triplet lifetimes as revealed by the nanosecond laser-flash photolysis exposes more about the competitive and predominant wastage process, i.e., radical recombination (k_{rc}, Scheme 3) operative for the aryl radicals of **5a**, which are highly electrophilic; it should be noted that methoxy groups are e-withdrawing for aryl σ-radicals and e-donating for π-radicals [8,24]. The fact that benzene–Br• complex is simply not observed from **5a** as well as **4a** attests to this caveat. In contrast, the situation with respect to moderately nucleophilic 2-aroylaryl radicals such as those generated from ketones **6a** and **10b** is not discouraging, for they undergo cyclization with moderate efficiency. Of course, hydrogen translocations followed by cyclization cannot be discounted in these cases. Otherwise, as shown in Scheme 3, the photochemical results of all ketones **1–11** (Chart 1) can be nicely rationalized within the extrema of reactivities represented by ketones **3a**,**b**,**5a**,**b**: moderately electrophilic radicals of **3a** exhibit radical translocations, radicals of **3b** and **5b**, which may stabilize via conversion to hydrofluorenyl radicals undergo cyclization, and highly electrophilic radicals of **5a** undergo radical recombination predominantly (Scheme 3).

CONCLUSIONS

We have investigated the steady-state photochemistry and nanosecond transient phenomena of a broad set of 2-bromoaryl ketones, whose structures are twisted as revealed by X-ray-determined crystal structures. The photolysis of ketones leads to cyclization products, viz., Fls, in varying yields via initial C–Br bond cleavage. The nanosecond laser-flash photolysis produces transients that are assigned to T–T absorptions; the latter are not readily comparable to those of simple BPs. The substituents produce varying degrees of influence on the T–T absorption spectra depending on which of the phenyl rings, i.e., Ph or BrPh, that they are part of. The origin of the observed T–T absorption bands can be rationalized by resonance effects that are complemented by structural insights from X-ray crystallographic analyses. By associating the triplet decays with C–Br bond cleavage rates, we have determined the absolute rate con-

stants for C–Br homolysis for a variety of substituted BPs. A difference in the rate constants by an order of magnitude was observed for all ketones that do not contain methoxy-substitutents at *meta* positions; the observed rate differences are likely to be due to variations in triplet excitation energies. Alternatively, by combining the insights from X-ray-determined molecular structures with transient decay analysis localization of excitation energy is proposed to account for the observed differences in the rates of C–Br homolysis.

The triplet decay rate constants and quantum yield measurements (for ketone disappearance) offer insights into the absolute kinetic rate data concerning C–Br homolysis and radical recombinations. The preparative photochemistry and transient phenomena permit invaluable inferences as to the reactivity of 2-aroylaryl radicals in general. Accordingly, highly electrophilic aryl radicals appear to undergo radical recombination, in a poor hydrogen-donating solvent, almost exclusively in the absence of incentive for stabilization via conversion to π-conjugated hydrofluorenyl radicals. Of course, when the latter is feasible, Pschorr cyclization leading to Fls is the predominant pathway. Moderately electrophilic radicals that are devoid of stabilization via conversion to hydrofluorenyl radicals lend themselves to intramolecular 1,5-hydrogen shifts. The aryl radicals in general may be generated by electron transfer, electrochemical reduction, tributylstannane-mediated halogen abstractions, etc. The reactivity of 2-aroylphenyl radicals established herein should be of general applicability for aryl radical cyclizations in organic synthesis.

EXPERIMENTAL SECTION

General procedure for preparative photolyses of ketone

A solution of 2-bromoketone (3–4 mM) in dry acetonitrile was taken in a pyrex tube, purged with N_2 gas for 30 min, and then irradiated in a Luzchem photoreactor fitted with $\lambda \approx 350$ nm lamps. Depending upon the substrate, the colorless solutions of the ketones turned into yellow or orange or greenish yellow color within 1 h of photoirradiation. The progress of the reaction in each case was monitored by (GC) and thin-layer chromatography (TLC) analysis. After photolysis, the solvent was removed in vacuo and the residue was dissolved in dichloromethane (DCM). The organic layer was thoroughly washed with saturated solution of K_2CO_3 in water, the solvent was removed in vacuo and the residue was subjected to a careful silica-gel column chromatography or radial chromatography on chromatotron to isolate the photoproducts, viz., regioisomeric Fls and the dehalogenated BP. Due to near equal polarity of regioisomaric Fl derivatives, dehalogenated BP and the starting 2-bromoketone, in some cases, the crude photolysates were subjected to $NaBH_4$ reduction to afford a mixture of alcohols, which were then separated by radial chromatography. The alcohols thus isolated were further oxidized with PCC to regenerate the ketones. All the Fl derivatives were characterized by spectroscopic data, cf. SI. All the dehalogenated ketones are reported in the literature, and they were characterized by comparison of their ^{1}H NMR spectral data with the literature data.

Determination of quantum yields

The quantum yields were determined using valerophenone as an actinometer ($\Phi_{313nm} = 0.33$ for the formation of AP) [14]. For quantum yield measurements, ca. 5.3–15.5 mM solutions of a ketones (**1a–d**,**2a**,**b**,**6a**) in acetonitrile containing a small amount of methyl benzoate as an internal standard were irradiated (313 nm) using a high-pressure Hg lamp (Applied Photophysics) equipped with a monochromator. Conversion of the ketones was limited to 4–12 % and analyses were performed by GC.

Laser-flash photolysis

Experiments were carried out with an LKS.60/S nanosecond laser-flash photolysis spectrometer (Applied Photophysics) with a GSI Lumonics Pulsemaster PM-846 excimer laser running on XeCl for excitation (308 nm, ca. 80 mJ pulse energy, 10 ns pulse width). The transient data were recorded with a 54830B 600 MHz Infinium oscilloscope (Agilent Technologies) and processed with the instrument-supplied software. Transient spectra were recorded in a step-scan mode in 10-nm intervals. Transient decay traces were recorded near the transient absorption maxima at ca. 320 and 450 nm. Samples (ca. 3 mL) were prepared in fused long-neck quartz cuvettes to allow bubbling with dry nitrogen gas for 15 min to remove oxygen. The optical densities of all samples were adjusted to 0.4 ± 0.1 at 308 nm using a Cary50 UV spectrophotometer (Varian Inc.).

X-ray crystal structure determinations

Good crystals of **1b** were obtained by slow evaporation of its solution in ethyl acetate-pet. ether (2:1). Similarly, good crystal of **1c** and **2a** were grown from a mixture of chloroform-pet. ether (1:2) and dichloromethane-pet. ether (2:1), respectively.

The crystals were mounted in a glass capillary, cooled to 100 K and the intensity data were collected on a Bruker Nonius SMART APEX CCD detector system with Mo-sealed Siemens diffraction tube (λ = 0.71073 Å) and a highly oriented graphite monochromator operating at 50 kV/30 mA. The lattice parameters and standard deviations were obtained by a least squares fit using 25 frames with 20 sec/frame exposure using the Bruker SMART software. The data were processed and reduced using SAINTPLUS and empirical absorption correction was made using Bruker SADABS. The structure was solved by Direct Methods using SHELXTL package, and refined by the full matrix least-squares based on F^2 using SHELX97 program. The hydrogen atoms were generally located from the difference Fourier. Wherever they were not located, they were fixed at ideal positions and included in the refinement.

SUPPLEMENTARY INFORMATION

Experimental details of synthesis and characterization, characterization details of photoproducts, transient absorption spectra, the plots for quenching kinetics, and X-ray crystal data are available online (doi:10.1351/PAC-CON-10-10-26).

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