Intramolecular Addition Reactions of Functionalized Arylcarbenes to Arenes

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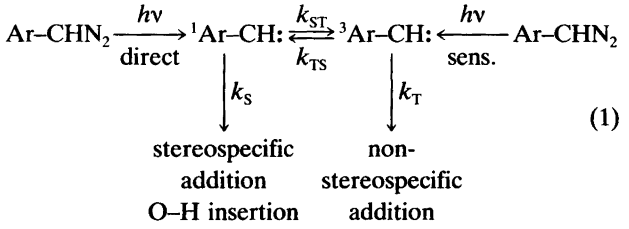
[2-(Arylmethyl)phenyl]carbenes with Ar = phenyl (**16**), 1-naphthyl (**20**), and 2-furyl (**24**) have been generated photolytically from appropriate diazo or tosylhydrazone precursors. Intramolecular addition to the arene prevailed in pentane solution, insertion into *ortho* C–H bonds of the arene being a minor process. On direct photolysis in methanol, intermolecular O–H insertion predominated over intramolecular addition to phenyl and 1-naphthyl groups ($k_S<k_{OH}$). The ratio of addition to O–H insertion was not affected by benzophenone sensitization in the case of Ar = Ph, but increased strongly in the case of Ar = 1-naphthyl. These data, implying $k_T>k_{TS}$ for **20**, constitute the first evidence for the addition of triplet arylcarbenes to arenes. Ar = 2-furyl was found to promote the intramolecular addition of both singlet **24** ($k_S \cong k_{OH}$) and triplet **24** ($k_T>k_{TS}$). The reactivity of arenes toward electrophiles (k_S) and the stabilization of diradical intermediates (k_T) is thought to account for the observed trends.

Dedicated to Professor Lars Skattebøl on the occasion of his 65th birthday.

It is widely believed that spin-state-specific mechanisms can be assigned to the reactions of carbenes. For example, many carbenes with heteroatoms attached directly to the central carbon have singlet ground states, the excited triplet states being experimentally inaccessible. These carbenes undergo concerted, stereospecific cycloadditions with alkenes and insert readily into O–H bonds.[1] Stepwise, non-stereospecific addition to alkenes and hydrogen-atom abstraction from alcohols are characteristic of carbenes that react from their triplet ground states, e.g. anthronylidene.[2,3] There are two chemically important states of methylene, $^1A_1$ and $^3B_2$. Singlet–triplet interconversion of methylene is slow enough for specific interception of each spin state.[1,4] In contrast, the spin equilibration of arylcarbenes appears to be rapid, relative to their intermolecular reactions. Moss and Dolling demonstrated that the stereospecificity of the addition of phenylcarbene to 2-butene was not diminished by dilution with perfluorobutane.[5] Creary found the benzophenone-sensitized reaction of phenyldiazomethane with (*Z*)-2-butene to be largely stereospecific.[6] We observed that the relative rates of O–H insertion and C=C addition of phenylcarbene in 2-butene–methanol mixtures were only slightly affected by sensitization[7] (Fig. 1).



(1)

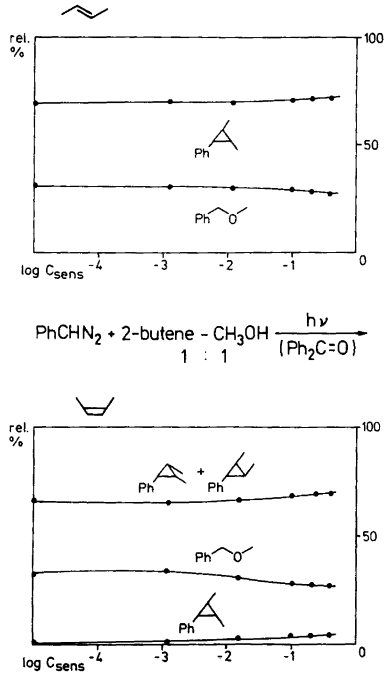
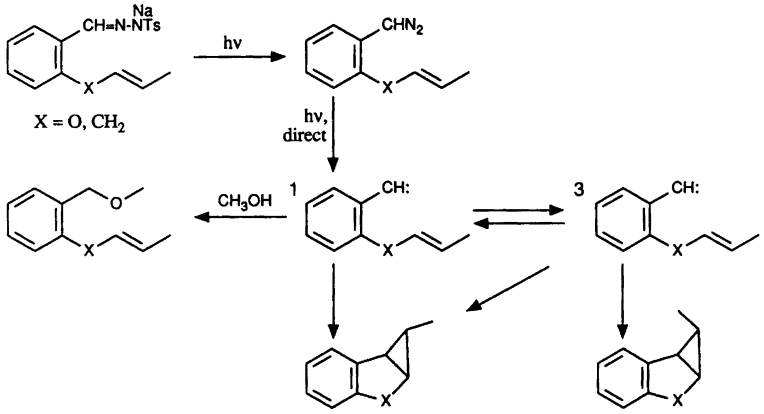


Fig. 1. Product distribution from the photolyses of phenyldiazomethane in equimolar mixtures of methanol and (*E*)-2-butene (upper) or (*Z*)-2-butene (lower).



Scheme 1.

Although the triplet has been shown to be the ground state of phenylcarbene by low-temperature EPR spectroscopy,[8] the *intermolecular* reactions appear to be channelled through the less abundant, but more reactive singlet state [$k_{TS}k_S > k_{ST}k_T$ in terms of eqn. (1)]. Recently we reported that these rules do not hold for *intramolecular* reactions.[7] Arylcarbenes with unsaturated *ortho* substituents (Scheme 1) were generated in methanol by photolysis of diazo precursors. Intermolecular O–H insertion to give benzyl ethers was found to predominate in direct photolyses. On sensitization, the fraction of ether decreased to below 10 %, with a concomitant increase of the intramolecular addition to more than 90 %. Addition to the internal double bond was moderately stereoselective in direct photolyses, and converged to give identical mixtures of *exo* and *endo* adducts on sensitization (Fig. 2). These observations imply that triplet arylcarbenes respond to the entropic benefits of intramolecularity while singlet arylcarbenes do not. The inefficient intramolecular addition of singlet arylcarbenes is attributed to their sizeable rotational barriers.[9] Singlet addition is initiated by an approach of the vacant p orbital to the π system which – in the case of Scheme 1 – cannot occur without rotation about the bond connecting the divalent carbon to the aryl ring. The triplet arylcarbene, on the other hand, may utilize the half-filled in-plane σ orbital in the first stage of the addition process, thus avoiding rotation.

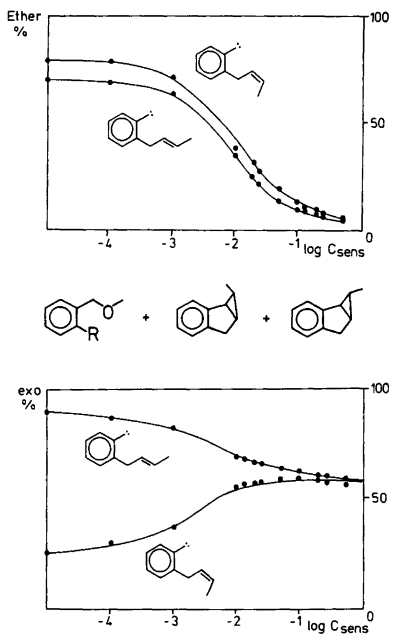
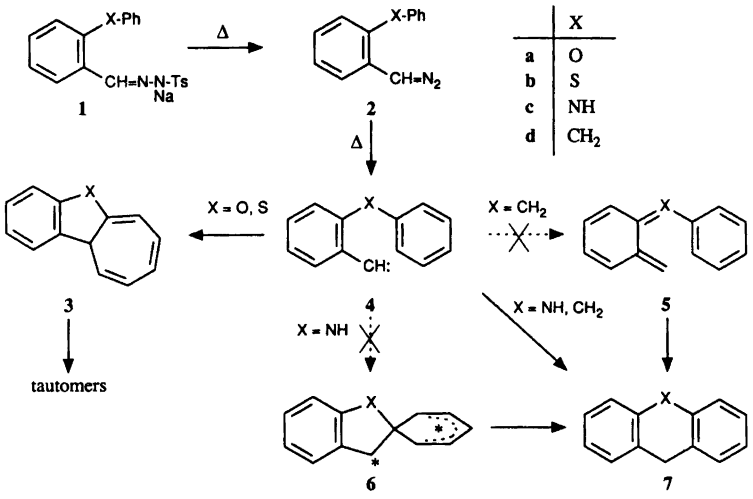


Fig. 2. Fraction of O–H insertion (upper) and distribution of epimeric cycloadducts (lower) from the photolyses of [2-(2-butenyl)phenyl]diazomethane in methanol (cf. Scheme 1).

In the present paper, we focus on intramolecular addition reactions of arylcarbenes to arenes. The arenes were positioned to replace the double bonds of the substrates shown in Scheme 1. Although intermolecular addition reactions of arylcarbenes to arenes are known,[10] the question of spin states has not been addressed, owing to the lack of stereochemical criteria. Examples of analogous intramolecular reactions are quite rare.[11] To our knowledge, the only relevant report on 2-(XC_6H_5)-substituted phenylcarbenes (**4**) came from Crow and McNab.[12] Thermolysis of the tosylhydrazone sodium salts **1** at 120 °C afforded the diazo compounds **2** which were then pyrolyzed at 500 °C in the gas phase (Scheme 2). The major reaction of **4a** (X = O) and **4b** (X = S) was addition to the π system, to give **3a,b** and tautomers derived therefrom by 1,5-H shifts. The carbenes **4c** (X = NH) and **4d** (X = CH_2), on the other hand, produced mainly dihydroacridine (**7c**) and dihydroanthracene (**7d**), respectively. The use of substituents showed that no spirodiene intermediate **6c** was involved in the case of X = NH. Deuterium labels excluded 1,4-hydrogen transfer, with intervention of **5d**, in the case of X = CH_2. The formation of **7** was therefore attributed to direct σ insertion into the *ortho* C–H bonds.

In our approach to the question of reacting spin states, analogous carbenes were generated in methanol as well as in aprotic solvents. Although stereochemical evidence cannot be adduced, competitive intramolecular addition and

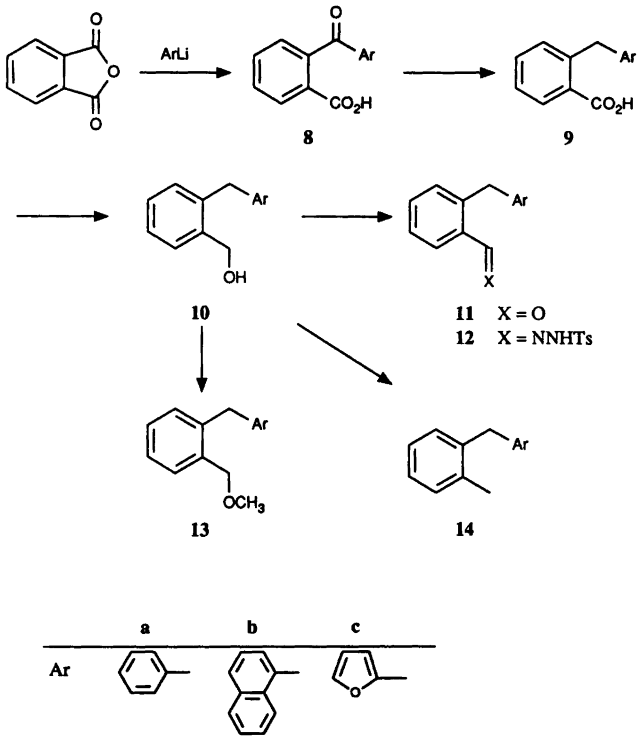


Scheme 2.

intermolecular O–H insertion should provide valid information (cf. the upper part of Fig. 2). Moreover, the character of the arene was varied from aromatic to olefinic-like by employing phenyl, 1-naphthyl, and 2-furyl groups.

Results and discussion

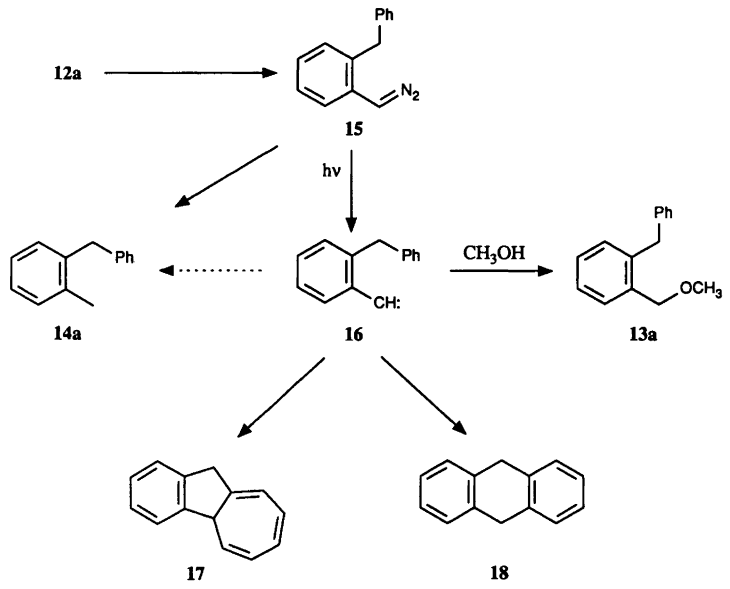
Synthesis. Carbene precursors were prepared by conventional routes, starting from phthalic anhydride and the appropriate aryllithium. The 2-aroylbenzoic acids (**8**) thus obtained were reduced with Zn/Cu to give 2-(arylmethyl)-benzoic acids (**9**). Reduction of **9** with $LiAlH_4$, to yield 2-(arylmethyl)benzyl alcohols (**10**), was followed by oxidation ($PCC–Al_2O_3$) to provide 2-(arylmethyl)benzaldehydes (**11**) and the tosylhydrazones **12** derived therefrom. The alcohols **10** were readily converted into the ethers **13** (NaH/CH_3I) and the hydrocarbons **14** (H_2/Pd–C) (Scheme 3). Samples of **13** and **14** were required for comparison with reaction products of **12** (see below).



Scheme 3.

(2-Benzylphenyl)carbene (**16**). The diazo compound **15** was obtained from the tosylhydrazone **12a** by a standard procedure[13] (50 % NaOH, dioxane, 90 °C). Photolysis of **15** in pentane produced 10*H*-benzo[*a*]azulene (**17**) as the major volatile product (Scheme 4). According to the NMR spectrum of **17**, the intramolecular adduct of **16** was isolated without isomerization due to 1,5 (thermal) or 1,7 (photochemical) shifts of hydrogen. 9,10-Dihydroanthracene (**18**) was a minor product of direct photolyses of **15**, and virtually absent in benzophenone-sensitized photolyses (Table 1). In contrast, previously reported thermolysis of **15** gave **18** exclusively.[12] The data indicate that **18** derives from the singlet state of **16** while the origin of **17** is less clearly defined (see below).

In order to study the competition of intramolecular addition and intermolecular O–H insertion, the tosylhydrazone **12a** was photolyzed in 0.1 M NaOMe–MeOH. The protic conditions led to the predominant formation of the benzyl ether **13a**, together with minor amounts of **14a** and **17** (Table 1). On sensitization, formation of **14a** increased at the expense of **13a** and **17**. Hydrogen abstraction by triplet **16** is an obvious route to **14a**, but probably not the only one. Controls with various aryldiazo compounds (including diphenyldiazomethane) revealed that the yields of hydrocarbons increase with the concentration of both sensitizer and base.[14] Deuterium from CH_3OD was incorporated into the hydrocarbons, contrary to expectations based on a triplet abstraction mechanism. Therefore, we suggest single electron transfer (SET) from the radical anion of the sensi-



Scheme 4.

Table 1. Distribution of products (%) derived from (2-benzylphenyl)carbene (**16**).

Precursor	Solvent	$[Ph_2CO]/M^{-1}$	**13a**	**14a**	**17**	**18**
15, *hv*	Pentane	0	–	<1	88.7	10.3
		0.2	–	<1	99	<1
12a, *hv*	0.1 M NaOMe–MeOH	0	81.9	5.2	12.7	<1
		0.01	82.9	8.4	8.7	–
		0.05	80.6	12.9	6.4	–
		0.1	78.0	14.5	7.4	–
		0.2	77.5	16.1	6.4	–

tizer[15] to the diazo compound as an alternative route, eqn. (2). The radical anions of diazo compounds, generated electronchemically, are known to give hydrocarbons with incorporation of protons (deuterons) from the solvent.[16]

$$^3Ph_2C{=}O^* \xrightarrow{R\text{–}H} Ph_2\dot{C}\text{–}OH \xrightarrow{CH_3O^-} Ph_2\dot{C}\text{–}O^-$$

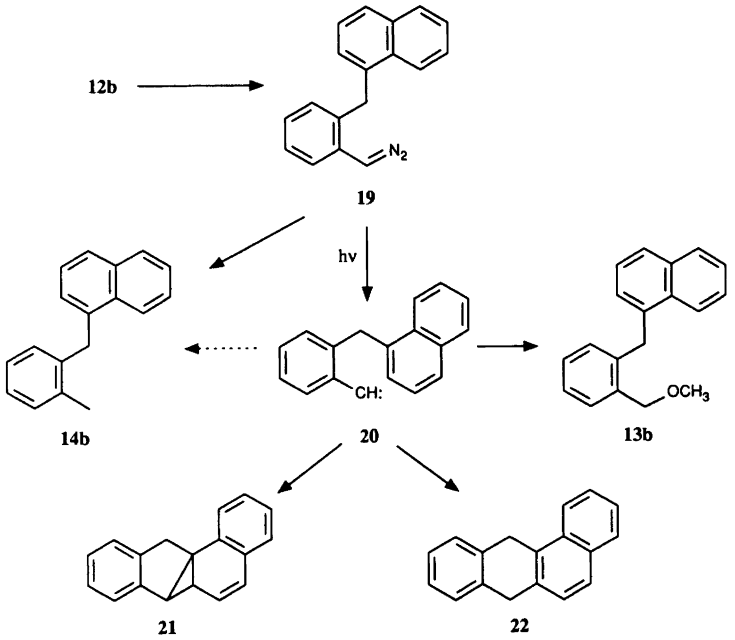
$$Ph_2\dot{C}\text{–}O^- + Ar\text{–}CHN_2 \longrightarrow Ph_2C{=}O + Ar\text{–}CHN_2^{\bullet -} \quad (2)$$

$$AR\text{–}CHN_2^{\bullet -} \xrightarrow{CH_3OH} N_2 + Ar\text{–}CH_3$$

The ratio of **13a** to **17** is only slightly affected by sensitization. The overall pattern resembles Fig. 1, rather than Fig. 2(a). In terms of eqn. (1), spin equilibration must proceed rapidly as compared with chemical reaction. Intramolecular addition of triplet **16** is not excluded, but turns out to be slow relative to intersystem crossing ($k_T < k_{TS}$). In methanol, the reaction is channeled largely through the singlet state to give **13a**. In the absence of an efficient singlet trap, i.e., in aprotic media, triplet **16** may well be the major source of **17**.

[2-(1-Naphthylmethyl)phenyl]carbene (**20**). The comparison of **20** with **16** reveals analogies as well as intriguing differences. Intramolecular addition of **20**, involving the 1,2 bond of the 1-naphthyl group, leads to the norcaradiene **21** (Scheme 5). Ample precedent may be found among intermolecular addition reactions of carbenes to naphthalene.[17] The norcaradiene structure of the adducts is preferred since the six-membered ring of the corresponding benzocycloheptatrienes would be quinoidal rather than aromatic. Intramolecular C–H insertion, with formation of **22**, amounts to less than 25 % of that observed with **16**. As before, only traces of C–H insertion products were observed in the presence of benzophenone and/or methanol (Table 2).

Direct photolyses of **12b** in MeOH–NaOMe gave a ratio of O–H insertion to intramolecular addition (**13b:21**) similar to that obtained from **12a**. Benzophenone sensitization, however, caused **21** formation to increase strongly, with a



Scheme 5.

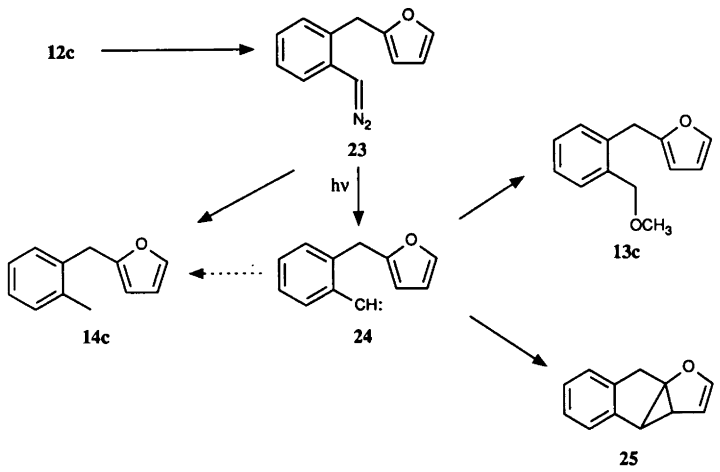
Table 2. Distribution of products (%) derived from [2-(1-naphthylmethyl)phenyl]carbene (**20**).

Precursor	Solvent	$[Ph_2CO]/M^{-1}$	**13b**	**14b**	**21**	**22**
19, *hv*	Pentane	0	–	6.0	91.5	2.5
		0.05	–	3.4	95.6	<1
12b, *hv*	0.1 M NaOMe–MeOH	0	83.0	8.4	8.6	<1
		0.005	62.5	4.0	33.5	–
		0.01	54.9	6.4	38.7	–
		0.05	41.3	8.4	50.3	–
		0.1	34.6	6.6	58.8	–
		0.2	26.9	8.1	65.0	–

concomitant decrease in the production of **13b**. The remarkable effect of sensitization is unparalleled in the behavior of **16**. Obviously, triplet **20** undergoes intramolecular addition at a faster rate than intersystem crossing ($k_T > k_{TS}$) while the reverse holds for **16**. It appears unlikely that the spin inversion rates (k_{TS}) of **16** and **20** should differ substantially. Therefore, the observed changes are most reasonably attributed to faster intramolecular addition (k_T) of triplet **20**, as compared with triplet **16**. Enhanced stabilization of the diradical intermediate is thought to be an important factor in accelerating the addition reaction of triplet **20**. The concerted addition of singlet **20** is not favored analogously, and remains inefficient, relative to intermolecular O–H insertion.

[2-(2-Furylmethyl)phenyl]carbene (**24**). To our knowledge, intermolecular addition reactions of arylcarbenes to furans have not been investigated. The intramolecular addition of **24** was found to proceed smoothly, with formation of **25** (Scheme 6). Rearrangements that are sometimes associated with the addition of carbonylcarbenes to furans[18] and thiophenes[19] were not observed with **24**. The product derived from **24** by intramolecular C–H insertion may have been a minor component (<2%) of direct photolysis in pentane, but was not identified.

The intramolecular addition of **24** was found to compete efficiently with O–H insertion. On direct photolysis of **12c** in 0.1 M NaOMe–MeOH, the ratio of **13c** to **25** was ca. 1:1 (Table 3) while analogous ratios from **12a,b** were ca. 10:1. Replacement of phenyl or 1-naphthyl with 2-furyl facilitates electrophilic attack on the arene, thus enhancing the intramolecular reactivity of the singlet carbene. The effect of sensitization is somewhat obscured by the abundant formation of the hydrocarbon **14c** (cf. discussion on **14a**). Nevertheless, the ratio of **13c** to **25** is seen to decrease and to approach a value (0.30) which is smaller than that found for **13b:21** (0.41). Therefore, our arguments concerning the reactivity of triplet **20** are similarly applicable to **24**. In the



Scheme 6.

Table 3. Distribution of products (%) derived from [2-(2-furylmethyl)phenyl]carbene (**24**).

Precursor	Solvent	$[Ph_2CO]/M^{-1}$	13c	14c	25
23, *hv*	Pentane	0	–	<1	>95
		0.05	–	<1	>98
12c, *hv*	0.1 M NaOMe–MeOH	0	51.6	3.3	45.1
		0.01	35.2	13.1	51.7
		0.03	23.5	22.3	54.2
		0.05	22.6	22.5	54.9
		0.07	21.8	22.4	55.8
		0.1	20.4	26.3	53.3
		0.2	15.7	31.6	52.7

case of **24**, the diradical intermediate of triplet addition is stabilized by conjugation with oxygen, as well as by delocalization.

Conclusions

The reaction pattern of [2-(arylmethyl)phenyl]carbenes depends strongly on the nature of the arene. In our analysis of these effects we presume that the rates of intermolecular O–H insertion (k_{OH}, diffusion-controlled in the case of diphenylcarbene[20]) and the rates of intersystem crossing (k_{TS}, k_{ST}) are not significantly affected by the remote arene. With Ar = Ph, the intramolecular addition of both the singlet and the triplet state is relatively slow ($k_S < k_{OH}$, $k_T < k_{TS}$). Ar = 1-naphthyl leads to enhanced triplet reactivity ($k_T > k_{TS}$) while singlet addition remains inefficient ($k_S < k_{OH}$). Ar = 2-furyl promotes the intramolecular addition of both spin states ($k_S \cong k_{OH}$, $k_T > k_{TS}$). These trends conform with expectations based on the reactivity of arenes toward electrophiles (k_S) and on the stability of diradical intermediates (k_T).

Experimental

General methods. Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. ^1H NMR spectra were obtained at 80 (Bruker WP 80) and 400 MHz (Bruker AM-400). Chemical shifts in $CDCl_3$ are reported in δ relative to tetramethylsilane as an internal standard, unless otherwise indicated. Gas chromatography (GC) was performed by the use of a Siemens Sichromat equipped with glass capillary columns. Varian Aerograph 920 instruments equipped with packed glass columns were used for preparative gas chromatography (PGC). High-pressure liquid chromatography (HPLC) was carried out with LDC (Milton Roy) chromatographs and refractometric detection.

2-(Phenylmethyl)benzaldehyde tosylhydrazone (**12a**). To 2-(phenylmethyl)benzyl alcohol (**10a**)[21] (0.60 g, 3 mmol) in dichloromethane (10 ml) was added pyridinium chlorochromate on alumina[22] (7.5 g, 6–7 mmol). The mixture was stirred for 2 h at room temperature. Solids were filtered off and washed with ether (2×10 ml). The combined solutions were dried ($MgSO_4$) and evaporated *in vacuo*. The residue was purified by flash chromatography on silica gel (pentane–ether 2:8) to give 0.44 g (74 %) of 2-(phenylmethyl) benzaldehyde (**11a**).[23] ^1H NMR (80 MHz, $CDCl_3$)[12]: δ 4.45 (2 H, s), 7.0–7.9 (9 H, m), 10.24 (1 H, s).

The tosylhydrazone **12a**[12] was obtained from **11a** (1.96 g, 10 mmol) and *p*-tolylsulfonylhydrazine (1.95 g, 10.5 mmol) in ethanol (15 ml) by heating to reflux for 15–20 min. Yield 2.16 g (59 %), m.p. 150–152 °C (lit.[12] 150–152 °C). ^1H NMR (80 MHz, C_6D_6): δ 1.81 (3 H, s), 3.80 (2 H, s), 6.6–7.8 (13 H, m), 7.85 (1 H, s), 7.95 (1 H, s).

To a solution of **12a** (0.36 g, 1 mmol) in dioxane (20 ml) was added 50 % aqueous sodium hydroxide (2 ml). The mixture was stirred vigorously at 90 °C for 1 h. After cooling to 20 °C, the organic phase was separated, and the

aqueous phase was washed with pentane. The combined organic phases were washed with water, dried ($MgSO_4$), and concentrated *in vacuo*. The residue (0.20 g, 95 %) of crude diazo compound **15** was used without further purification.

Photolyses of **12a** *and* **15**. A solution of crude **15** (0.10 g) in pentane (20 ml) was purged with nitrogen and irradiated with a medium-pressure mercury lamp (Pyrex vessel, 15–20 °C, 1 h). After evaporation, 10 *H*-benzo[*a*]azulene (**17**) was isolated by HPLC (Polygosil 60-5-NO_2, ether–pentane 1:1). Yield 27 mg (30 %); Anal. $C_{14}H_{12}$: C, H. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.50 (1 H, br s, 8a-H), 3.95 (2 H, br s, 3-H), 5.15 (1 H, dd, *J* 9.5 and 4 Hz, 8-H), 6.12 (1 H, ddd, *J* 9.5, 5.5 and 2 Hz, 7-H), 6.30 (1 H, m, 4-H), 6.55 (1 H, dd, *J* 11 and 5.5 Hz, 5-H), 6.62 (1 H, dd, *J* 11 and 5.5 Hz, 6-H), 7.0–7.4 (4 H, m). The assignments were confirmed by H/H-COSY. 9,10-Dihydroanthracene (**18**) and 2-(phenylmethyl)toluene (**14a**)[12,24] were identified by comparison with authentic samples.

Solutions of **12a** (100 mg, 0.28 mmol) in 0.1 M NaOMe–MeOH (10 ml) were photolyzed analogously. The mixture was diluted with water (50 ml) and extracted with ether (3×15 ml).The combined organic extracts were dried ($MgSO_4$), concentrated, and analyzed by GC (Table 1). 1-(Methoxymethyl)-2-(phenylmethyl)benzene (**13a**), a major product of these photolyses, was prepared by methylation of **10a** (NaH, CH_3I, THF, 1 h reflux). Anal. $C_{15}H_{16}O$: C, H. ^{1}H NMR (80 MHz, $CDCl_3$): δ 3.42 (3 H, s), 4.15 (2 H, s), 4.49 (2 H, s), 7.0–7.6 (9 H, m).

2-(1-Naphthylmethyl)benzaldehyde tosylhydrazone (**12b**). A solution of 2-(1-naphthylmethyl)benzoic acid (**9b**)[25] (1.25 g, 4.7 mmol) in anhydrous ether (50 ml) was added to lithium aluminium hydride (0.38 g, 10 mmol) in ether (50 ml). The mixture was heated at reflux for 1.5 h. Conventional work-up afforded 0.80 g (68 %) of 2-(1-naphthylmethyl)benzyl alcohol (**10b**), m.p. 107 °C (recrystallized from hexane–ether). ^{1}H NMR (80 MHz, CD_3COCD_3): δ 4.55 (2 H, s), 4.75 (2 H, s), 6.8–7.6 (8 H, m), 7.7–8.15 (3 H, m).

Following the procedure described above for **10a**, the alcohol **10b** (5.3 g, 21 mmol) was oxidized to give 2-(1-naphthylmethyl)benzaldehyde (**11b**) (3.3 g, 63 %). ^{1}H NMR (80 MHz, $CDCl_3$): δ 4.95 (2 H, s), 7.0–7.6 (7 H, m), 7.7–8.15 (4 H, m), 10.3 (1 H, s). Heating of **11b** (3.3 g, 13 mmol) and *p*-tolylsulfonylhydrazine (2.6 g, 14 mmol) in ethanol (100 ml) at reflux for 30 min afforded the tosylhydrazone **12b** (5.1 g, 95 %), m.p. 162–163 °C (recrystallized from ethanol). Anal. $C_{25}H_{22}N_2O_2S$: C, H, N. ^{1}H NMR (80 MHz, C_6D_6): δ 1.53 (3 H, s), 4.50 (2 H, s), 6.85–8.0 (17 H, m).

The procedures described above for **12a** were performed on **12b** and **19**. The products obtained by photolysis of **19** in pentane were separated by HPLC (Polygosil 60-5-NO_2, ether–pentane 1:1). 6a*H*,12*H*-indeno[2′,1′:1.3]cyclopropa[1,2-*a*]naphthalene (**21**) was obtained pure (> 98 %, GC) by repeated HPLC (ether–pentane 1:99). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.33 (1 H, dd, *J* 3 and 1.5 Hz), 1.40 (1 H, dd, *J* 5 and 3 Hz), 2.77 (1 H, d, *J* 16.5 Hz), 3.80 (1 H, d, *J* 16.5 Hz), 6.10 (1 H, dd, *J* 10 and 5 Hz), 6.23 (1 H, d, *J* 10 Hz), 7.0–7.3 (8 H, m). Samples of **14b**[26] and **22**[27] were prepared according to the reported procedures. Methylation of **10b** (NaH, CH_3I, THF, 30 min reflux) afforded 1-(methoxymethyl)-2-(1-naphthylmethyl)benzene (**13b**). Anal. $C_{19}H_{18}O$: C, H. ^{1}H NMR (80 MHz, C_6D_6): δ 3.10 (3 H, s), 4.31 (2 H, s), 4.38 (2 H, s), 6.9–7.78 (10 H, m), 7.88–8.05 (1 H, m).

2-(2-Furylmethyl)benzaldehyde tosylhydrazone (**12c**). 2-(2-Furylmethyl)benzoic acid (**9c**)[28] (4.1 g, 20 mmol) was reduced with $LiAlH_4$ (1.52 g, 40 mmol) in ether (200 ml), as described above for **9b**, to give 2-(2-furylmethyl)benzyl alcohol (**10c**). Yield 2.98 g (72 %), ^{1}H NMR (80 MHz, $CDCl_3$): δ 1.98 (1 H, s), 4.05 (2 H, s), 4.70 (2 H, s), 5.95 (1 H, m), 6.28 (1 H, dd, *J* and 2 Hz), 7.15–7.5 (5 H, m).

Oxidation of **10c** (2.1 g, 11 mmol) with PCC–Al_2O_3 (75 g, 60–70 mmol) afforded 2-(2-furylmethyl)benzaldehyde (**11c**) (see the procedure for **10a**). yield 1.75 g (85 %); ^{1}H NMR (80 MHz, CD_3COCD_3): δ 4.48 (2 H, s), 6.02 (1 H, m), 6.30 (1 H, dd, *J* 4 and 2 Hz), 7.2–7.7 (4 H, m), 7.8–7.96 (1 H, m), 10.33 (1 H, s). The tosylhydrazone **12c** was prepared from **11c** (1.75 g, 9 mmol) and *p*-tolylsulfonylhydrazine (1.85 g, 10 mmol) in ethanol (20 ml, 20 min heating at reflux). Yield 2.34 g (70 %), m.p. 124 °C. Anal. $C_{19}H_{18}N_2O_3S$: C, H, N. ^{1}H NMR (80 MHz, $CDCl_3$): δ 2.40 (3 H, s), 4.05 (2 H, s), 5.82 (1 H, d, *J* 4 Hz), 6.20 (1 H, dd, *J* 4 and 2 Hz), 7.1–7.38 (6 H, m), 7.62–7.9 (4 H, m), 8.0 (1 H, s).

The procedures described above for **12a** were applied to **12c** and **23**. A solution of the diazo compound **23** in pentane, prepared from 355 mg (1.0 mmol) of **12c**, was irradiated for 90 min. Following the directions given for **21**, 3a*H*,9*H*-indeno[2′,1′:1,3]cyclopropa[1,2-*b*]furan (**25**) was isolated and purified by HPLC. Anal. $C_{12}H_{10}O$: C, H. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.61 (1 H, br s), 1.92 (1 H, br s), 3.32 (1 H, d, *J* 17 Hz), 3.75 (1 H, d, *J* 17 Hz), 5.48 (1 H, td, *J* 2.5 and 1 Hz), 6.52 (1 H, d, *J* 2.5 Hz), 7.1–7.3 (4 H, m). Methylation of **10c** (NaH, CH_3I, THF, 30 min reflux) afforded 1-(furylmethyl)-2-(methoxymethyl)benzene (**13c**). Anal. $C_{13}H_{14}O_2$: C, H. ^{1}H NMR (80 MHz, $CDCl_3$): δ 3.38 (3 H, s), 4.04 (2 H, s), 4.50 (2 H, s), 5.92 (1 H, d, *J* 4 Hz), 6.25 (1 H, dd, *J* 4 and 2 Hz), 7.18–7.4 (5 H, m). A sample of 2-(2-furylmethyl)toluene (**14c**) was prepared by a Wurtz-type reaction of 2-furyllithium, obtained from 2.5 ml (34 mmol) of furan and 9.3 ml of 1.6 M butyllithium in 20 ml of ether at −78 °C, with 6.3 g (34 mmol) of 2-methylbenzyl bromide (12 h at 20 °C). The product was purified by PGC (DC 200, 150 °C). Anal. $C_{12}H_{12}O$: C, H. ^{1}H NMR (80 MHz, $CDCl_3$): δ 2.30 (3 H, s), 3.95 (2 H, s), 5.88 (1 H, d, *J* 4 Hz), 6.25 (1 H, dd, *J* 4 and 2 Hz), 7.05–7.38 (5 H, m).

References

1. For reviews, see: (a) Regitz, M., Ed. *Carben(oide), Carbine*, Houben-Wyl, Vol. E 19b, Thieme, Stuttgart 1989; (b) Wentrup, C. *Reactive Molecules*, Wiley, New York 1984, Chap. 4; (c) Moss, R. A., Jones, M. Jr., Eds. *Carbenes*, Vols. I, II, Wiley, New York 1973, 1975; (d) Kirmse, W. *Carbene Chemistry*, 2nd. ed., Academic Press, New York 1971, Chap. 8.
2. Schuster, G. B. *Adv. Phys. Org. Chem. 22* (1986) 311.
3. Field, K. W. and Schuster, G. B. *J. Org. Chem. 53* (1988) 4000.
4. Turro, N. J., Cha, Y. and Gould, I. R. *J. Am. Chem. Soc. 109* (1987) 2101, and references cited therein.
5. Moss, R. A. and Dolling, U.-H. *J. Am. Chem. Soc. 93* (1971) 954.
6. Creary, X. *J. Am. Chem. Soc. 102* (1980) 1611.
7. Kirmse, W. and Hömberger, G. *J. Am. Chem. Soc. 113* (1991) 3925.
8. (a) Trozzolo, A. M., Murray, R. W. and Wasserman, E. *J. Am. Chem. Soc. 84* (1962) 4991; (b) Wasserman, E., Trozzolo, A. M., Yager, W. A. and Murray, R. W. *J. Chem. Phys. 40* (1964) 2408; (c) Barash, L., Wasserman, E. and Yager, W. A. *J. Am. Chem. Soc. 89* (1967) 770; (d) Moser, R. E., Fritsch, J. M. and Matthews, C. N. *Chem. Commun.* (1967) 770.
9. Dorigo, A. E., Li, Y. and Houk, K. N. *J. Am. Chem. Soc. 111* (1989) 6942.
10. (a) Ref. 1(a), pp. 922–927; (b) Ref. 1(d), pp. 386–387.
11. (a) The intramolecular adduct from [2-(3-phenylpropyl)-phenyl]carbene was not identified unambiguously: Gutsche, C. D., Jason, E. F., Coffey, R. S. and Johnson, H. E. *J. Am. Chem. Soc. 80* (1958) 5756; (b) Intramolecular additions of phenylcarbene to the benzene ring of 2-$CH_2SiPhMe_2$ and 2-$CH_2Si(CH_2Ph)Me_2$ groups have been reported: Kirmse, W. and Konrad, W. *Angew. Chem., Int. Ed. Engl. 29* (1990) 661.
12. Crow, W. D. and McNab, H. *Aust. J. Chem. 34* (1981) 1037.
13. Jonczyk, A. and Wlowstowska, J. *Synth. Commun. 8* (1978) 569.
14. Özkir, I. S. *Unpublished results.*
15. For a review, see: Cohen, T. *Tetrahedron 42* (1986) 2803.
16. (a) McDonald, R. N., Triebe, F. M., January, J. R., Borhani, K. J. and Hawley, M. D. *J. Am. Chem. Soc. 102* (1980) 7867; (b) See also: Bethell, D. and Parker, V. D. *Acc. Chem. Res. 21* (1988) 400.
17. Ref. 1(d), pp. 381–395.
18. (a) Schenck, G. O. and Steinmetz, R. *Justus Liebigs Ann. Chem. 668* (1963) 19; (b) Wenkert, E., Bakuzis, M. L. F., Buckwalter, B. L. and Woodgate, P. D. *Synth. Commun. 11* (1981) 533.
19. Storflor, H., Skramstad, J. and Nordenson, S. *J. Chem. Soc., Chem. Commun.* (1984) 208.
20. (a) Eisenthal, K. B., Turro, N. J., Aikawa, M., Butcher, J. A., Jr., DuPuy, C., Hefferon, G., Hetherington, W., Korenowski, G. M. and McAuliffe, M. J. *J. Am. Chem. Soc. 102* (1980) 6563; (b) Eisenthal, K. B., Turro, N. J., Sitzmann, E. V., Gould, I. R., Hefferon, G., Langan, J. and Cha, Y. *Tetrahedron 41* (1985) 1543.
21. Brasen, W. R. and Hauser, C. R. *J. Am. Chem. Soc. 77* (1955) 4158. Commercially available from Aldrich.
22. Cheng, Y.-S., Liu, W.-L. and Chen, S. *Synthesis* (1980) 223.
23. (a) Durst, T., Kozma, E. C. and Charlton, J. L. *J. Am. Chem. Soc. 50* (1985) 4829; (b) Woning, J., Lijten, F. A. T. and Larhoven, W. H. *J. Org. Chem. 56* (1991) 2427.
24. Uemura, S., Tanaka, S. and Okano, M. *J. Chem. Soc., Perkin Trans. 1* (1976) 1966.
25. Bergmann, E. D. and Loewenthal, E. *Bull. Soc. Chim. Fr.* (1952) 66.
26. (a) Gribble, G. W., Kelly, W. K. and Emery, S. E. *Synthesis* (1978) 763; (b) Lee-Ruff, E., Hopkinson, A. C., Kazarians-Moghaddam, H., Gupta, B. and Katz, M. *Can. J. Chem. 60* (1982) 154.
27. (a) Harvey, R. G. and Urberg, K. *J. Org. Chem. 33* (1968) 2206; (b) Fu, P. P., Lee, H. M. and Harvey, R. G. *J. Org. Chem. 45* (1980) 2797.
28. Lopes, C. C., Lopes, R. S. C., Pinto, A. V. and Costa, P. R. R. *J. Heterocycl. Chem. 21* (1984) 621.

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