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INTRAMOLECULAR REACTIVITY OF ARYLCARBENES: BIPHENYL-2-YLCARBENES

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Biphenyl-2-ylcarbenes, 2-ArC_6H_4CR, were generated photolytically and thermally from diazo precursors. Cyclization, leading to fluorenes, competes with capture of the carbenes by methanol but proceeds faster than intramolecular hydrogen shifts (with R = Me) and intermolecular C—H insertion reactions (with R = H in cyclohexane). By comparison of product ratios with kinetic data for related carbenes from the literature, the cyclization rate is estimated as *ca* 10^{11} s^{-1}. The intramolecular reactivity of biphenyl-2-ylcarbenes is not significantly attenuated by variation of R (R = H, Me, Ph). Very minor effects of triplet sensitization and methanol quenching indicate that fluorenes arise from spin-equilibrated biphenyl-2-ylcarbenes, presumably from the singlet state. When Ar = mesityl, the carbene predominantly inserts into C—H bonds of the 2′-methyl groups, giving rise to a dihydrophenanthrene. Formation of a fluorene derivative, by formal insertion into C—C bonds, occurs as a minor process. This unprecedented reaction points to intervention of an *o*-xylylene in which the methyl group migrates. Laser flash photolysis (LFP) of 2-$PhC_6H_4CN_2Ph$ generates a transient absorption which is due to the $T_0 \rightarrow T_n$ transition of 9-phenylfluorene rather than to the presumed *o*-xylylene. On LFP of 2-$ArC_6H_4CN_2Ph$ in trifluoroethanol–acetonitrile, protonation of the carbenes gives rise to carbocations, 2-$ArC_6H_4CH^+Ph$. The transient absorption spectra of these cations are strongly influenced by twisting about the Ar—Ar bond (Ar = Ph < *o*-tolyl < mesityl) whereas the rates of nucleophilic capture vary only slightly. Biphenyl-2-ylcarbenium ions (Ar = R = Ph) cyclize more slowly than the analogous carbenes, by a factor of ≥10^4.

INTRODUCTION

Arylcarbenes are known to interact readily with functional groups incorporated in or attached to *ortho* side-chains (C—H bonds,[1] alkenes,[2] arenes[3] and heteroatoms[3c,4]). Reactions leading to five-membered rings mostly proceed from the triplet state,[1g-i,2] whereas singlet reactions compete or prevail in the formation of six-membered rings.[3d,4d] These observations have been explained in terms of the enhanced steric constraints of concerted singlet reactions, as compared with stepwise triplet reactions. Owing to rapid singlet⇌triplet equilibration, the multiplicity of *reacting* arylcarbenes is influenced by the specific transition state geometry rather than by the mode of generation. On the other hand, the course of most intramolecular reactions is unexceptional; thus insertion into C—H and O—H bonds, cyclopropanation of alkenes and ylide formation with heteroatoms have been observed.

In contrast, the intramolecular reactivity of biphenyl-2-ylcarbenes is unique and without parallel among intermolecular reactions of arylcarbenes. As a rule, arylcarbenes add to arenes with the formation of norcaradienes and/or cycloheptatrienes.[5] Prohibitive strain would develop in an analogous intramolecular reaction of biphenyl-2-ylcarbenes. In fact, photolysis of 2-diazomethylbiphenyl (**1**) in solution affords fluorene (**3**), along with small amounts of solvent-derived products (**4**).[6,7] Since the deuterium isotope effect of the formal C—H insertion is very small ($k_H/k_D = 1{\cdot}12$),[6] rate-controlling cyclization of biphenyl-2-ylcarbene (**2**) to give a diradical (**5**) or *o*-xylylene (**6**) is thought to be followed by migration of hydrogen (Scheme 1). Product ratios indicate that the cyclization of **2** is about as fast as the intermolecular O—H insertion with methanol[8] and 19 times faster than the intermolecular C—H insertion with cyclohexane. The *relative* reactivities of **2** towards methanol and cyclohexane agree closely with kinetic data obtained for 1-naphthylcarbene ($k_{MeOH}/k_{cyclohexane} = 17{\cdot}9$).[9] If we assume that the *absolute* rates of **2** are also similar to those measured for 1-naphthylcarbene, we estimate $k_{2,3} \approx 2 \times 10^8$ s^{-1} for the triplet state of **2** and $k_{2,3} \approx 10^{11}$ s^{-1} for the singlet state (the latter estimate is based on a diffusional reaction with methanol, $k = 5 \times 10^9$ $M^{-1}s^{-1}$, as determined for diphenylcarbene[10]). These estimates, although admittedly crude, attest to rapid cyclization of biphenyl-2-ylcarbene (**2**).

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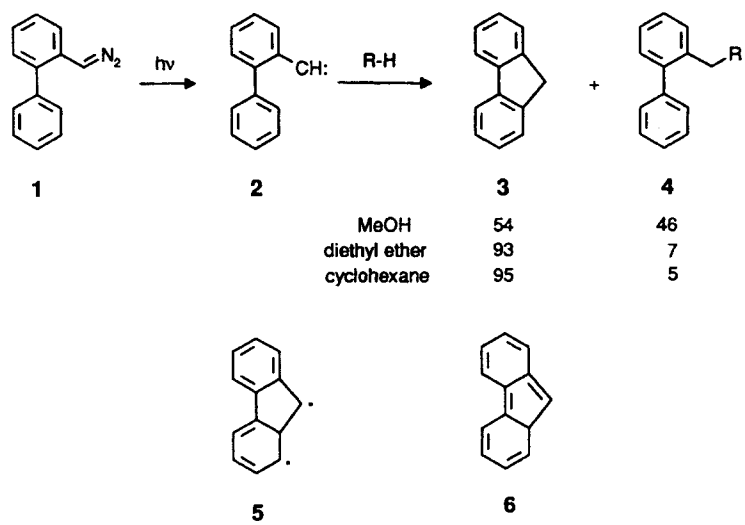


Scheme 1

The ESR spectrum of triplet **2** has been observed in low-temperature glasses at 77 K.[7] These conditions favour the abstraction of hydrogen, if available, from matrix molecules. However, substantial decay of **2** in perfluorinated alkane matrices points to cyclization even at 77 K. It is not clear whether the mechanism involves triplet addition to the *ortho* phenyl ring or whether the reaction proceeds through the small population of singlet carbene.

The objective of the present work was to explore the cyclization of biphenyl-2-ylcarbenes in more detail, through structural variations and application of laser flash photolysis (LFP).

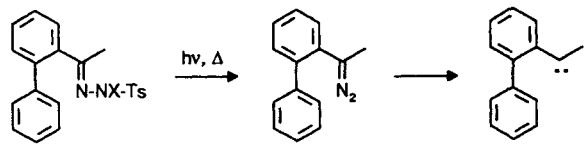
RESULTS AND DISCUSSION

1-(Biphenyl-2-yl)ethylidene (10)

The chemistry of 1-phenylethylidene is more complex than that of phenylcarbene. Styrene is the only product if intermolecular reaction paths are excluded, e.g. in the gas-phase pyrolysis of 1-phenyldiazoethane.[11] The 1,2 hydrogen shift leading to styrene has also been studied with matrix-isolated triplet 1-phenylethylidene at 65 K [$k = 2{\cdot}9 \times 10^{-4}$ s^{-1}, $\Delta G\ddagger = 4{\cdot}7$ kcal mol^{-1} (1 kcal = 4·184 kJ)].[12] Photolyses of 1-phenyldiazoethane in solution, on the other hand, give largely azine and/or solvent-derived products.[13,14] Acetonitrile is exceptional in giving high yields of styrene at room temperature with little evidence for side reactions. LFP studies of 1-phenylethylidene in acetonitrile led to $k_T = 6{\cdot}15 \times 10^6$ s^{-1}, $\Delta G\ddagger = 4{\cdot}4$ kcal mol^{-1} for isomerization of the triplet state and $k_S = 2{\cdot}0 \times 10^8$ s^{-1}, $\Delta G\ddagger = 2{\cdot}3$ kcal mol^{-1} for the singlet state.[14]

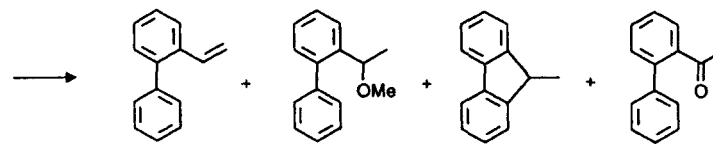
In view of these reports, we were interested in the relative rates of cyclization and 1,2 hydrogen shift for 1-(biphenyl-2-yl)ethylidene (**10**). The instability of the diazo compound **9** prompted us to use the tosylhydrazone salt **8** as the carbene precursor. This technique also serves to minimize the formation of azine, owing to small stationary concentrations of **9**. The products recorded in Scheme 2 were identified by comparison with authentic samples. Small amounts of 2-ethylbiphenyl were also observed, particularly when **8** was photolysed in methanol (1·9%). The formation alkylarenes does not necessarily involve arylcarbenes, as discussed elsewhere.[3d]

Cyclization leading to 9-methylfluorene (**13**) is the major reaction path of **10**, although the formation of 2-ethenylbiphenyl (**11**) competes to a minor extent (Scheme 2). If the **13**:**11** ratio is evaluated with the kinetic data for 1-phenylethylidene, the cyclization rate of triplet **10** ($k_{10,13} \approx 8 \times 10^7$ s^{-1}) is found to be in reasonable agreement with that of **2**. The analogous estimate for singlet **10** ($k_{10,13} \approx 2 \times 10^9$ s^{-1}), however, is not compatible with the **13**:**12** ratio obtained in methanol. The cyclization of **10** should be *ca* 100 times faster in order to compete with diffusional capture by methanol. Moreover, the yields of **11** respond strongly to triplet sensitization and singlet quenching by MeOH, whereas those of **13** are largely unaffected. These findings suggest that **11** and **13** arise from different intermediates. There is ample evidence that carbenic hydrogen shifts can be 'mimicked' by carbene precursors, such as (excited) diazo compounds.[15] In such cases, the product distributions do not correlate with the rate constants obtained by monitoring the carbene.



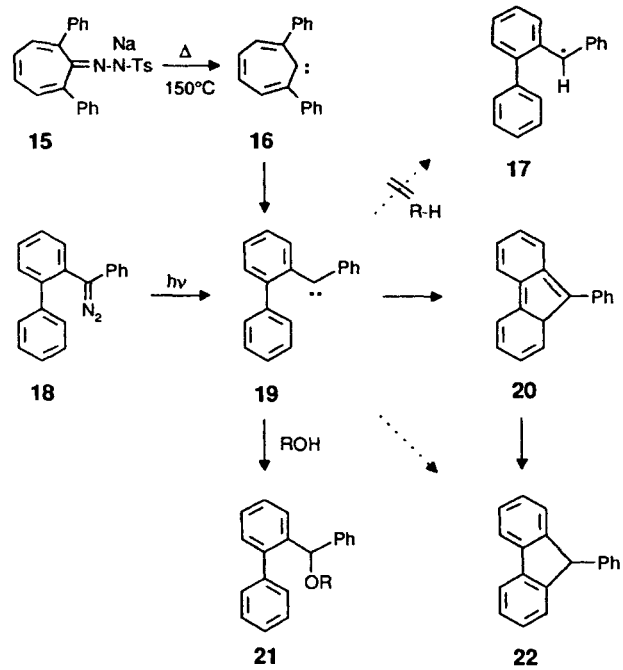
7 X = H
8 X = Na

9 **10**



	11	**12**	**13**	**14**
Δ, 300°C	12.9	-	87.1	-
hv, C_6H_6	6.8	-	84.6	8.4
hv, C_6H_6, Ph_2CO	0.7	-	77.8	21.5
hv, MeOH	*trace*	23.0	75.1	*trace*

Scheme 2



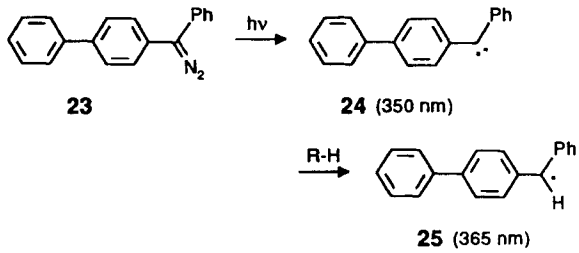
MeOH, hv	65	35
MeOH, hv, Ph_2CO	68	32
MeCN-TFE (1:1.6), hv	51	49

Scheme 3

(Biphenyl-2-yl)phenylcarbene (19)

An indirect route to **19** has been reported. Pyrolysis of the tosylhydrazone salt **15** was found to give 9-phenylfluorene (**22**), presumably via ring contraction of **16** and cyclization of **19** (Scheme 3).[16] On photolysis of the diazo compound **18** in aprotic media (benzene, acetonitrile), we obtained **22** as the only product. In the presence of alcohols, the ethers **21** were formed competitively with **22**. The fraction of **22** was not significantly affected by sensitization (Scheme 3). Since **18** did not persist in neat 2,2,2-trifluoroethanol (TFE), an acetonitrile–TFE (1 : 1·6) mixture, [TFE] ≈ 8·5 M, was used. Comparison with neat methanol (24·7 M) indicates that TFE is more reactive toward **19** than methanol, in accordance with a proton transfer mechanism.[17]

Before we discuss the LFP of **18**, a brief look at the *para* isomer **23** is in order. LFP of **23** in aprotic media generates the transient absorption of the triplet carbene **24** (λ_{max} = 350 nm).[18] As this band disappears, an absorption with λ_{max} = 365 nm grows in, which is assigned to the radical **25** (the same absorption is generated on LFP of the analogous chloride). Neither triplet **24** nor **25** is observed on LFP of **23** in methanol, owing to rapid quenching of singlet **24**. As would be expected, the LFP of **23** parallels that of diphenyldiazomethane.[19]



In contrast, LFP of **18** generates a transient absorption with λ_{max} = 370 nm (Figure 1) whose rates of decay ($k = 3{\cdot}4 \times 10^5$ s^{-1} in acetonitrile, $2{\cdot}4 \times 10^5$ s^{-1} in cyclohexane and $2{\cdot}3 \times 10^5$ s^{-1} in methanol) are nearly independent of the solvent. The presence of oxygen, however, has a strong accelerating effect. The decrease

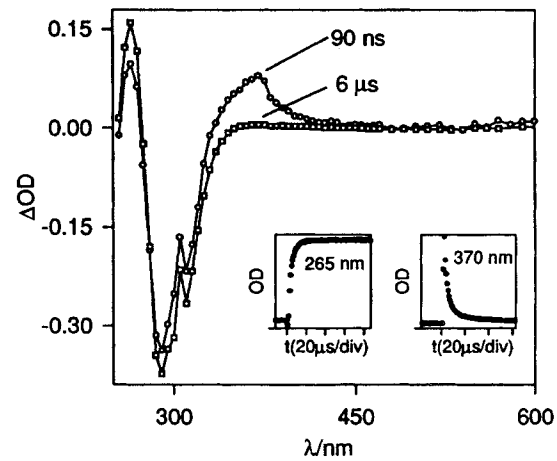
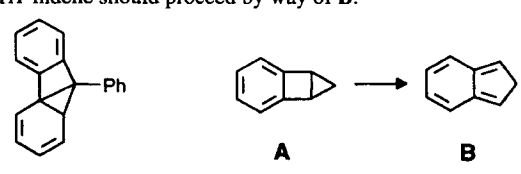


Figure 1. Time-dependent absorption spectra obtained after laser excitation (248 nm, 20 ns, 100 mJ per pulse) of **18** (0·1 nM) in argon-saturated acetonitrile. Insets: kinetic traces recorded at 265 and 370 nm

in optical density at 370 nm is associated with an increase at 265 nm, consistent with the eventual formation of **22** (λ_{max} = 266 nm, ε = 15 015). The slow reaction of the 370 nm transient with methanol argues against triplet **19** as the absorbing species ($k_{MeOH} = 6{\cdot}4 \times 10^6$ M^{-1}s^{-1} for triplet diphenylcarbene and $3{\cdot}6 \times 10^7$ M^{-1}s^{-1} for triplet **24**).[19] The radical **17** (λ_{max} = 335 nm, see Figure 2) is clearly excluded by its deviating absorption. The *o*-xylylene **20**, a likely intermediate en route to **22**, is less readily discounted. It appears, however, that neither the 370 nm absorption nor the small kinetic isotope effect (k_H/k_D = 1·6) observed on LFP of **18**-d_5 is compatible with **20**.* 1,2,3-Triphenyl-2*H*-indene (**26**)[20] is a reasonable model for **20**, two phenyl groups in **26** replacing double bonds in **20**. The absorption of **26** (λ_{max} = 478 nm) and the kinetic isotope effect (k_H/k_D = 3·7) of the **26**→**27** transformation differ strongly from what we observe on LFP of **18** and **18**-d_5. We assign the 370 nm band to triplet 9-phenylfluorene (^{3}**22**) since the same absorption is generated by laser excitation of **22**

*A reviewer suggested the intermediacy of **20'**, a valence tautomer of **20**. The relevant substructures of **20'** and **20** are tricylco[4·3·0·0^{7,9}]nona-1,3,5-triene (**A**) and 2*H*-indene (**B**), respectively. All available evidence indicates that **A** is less stable than **B**, and that the isomerization of **A** to 1*H*-indene should proceed by way of **B**.[24b,c]



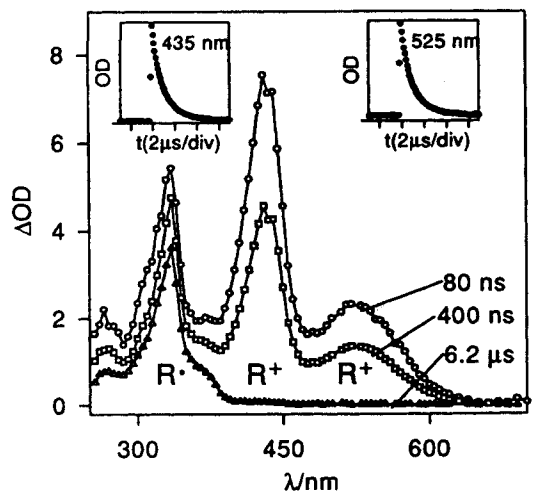
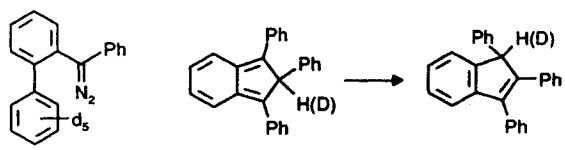


Figure 2. Time-dependent absorption spectra obtained after laser excitation (248 nm, 20 ns, 100 mJ per pulse) of **43** (0·22 mM) in argon-saturated acetonitrile. Insets: kinetic traces recorded at 435 and 525 nm

($S_0 + h\nu \longrightarrow S_1 \longrightarrow T_0$; $T_0 + h\nu \longrightarrow T_n$). Moreover, our data are in excellent agreement with those reported for triplet 9-fluorenol ($\lambda_{max} = 370$ nm, $k \approx 3{\cdot}7 \times 10^5\ s^{-1}$ in MeCN).[21] Deuteration of arenes is known to enhance the lifetimes of their lowest triplet states.[22]



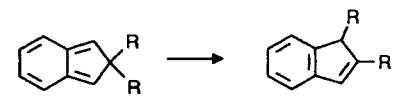
18-d_5 **26** **27**

9-Phenylfluorene (**22**) must be formed during the laser pulse (20 ns) in order for its $T_0 \longrightarrow T_n$ absorption to be observed. In the case of a stepwise mechanism (Scheme 3), both the cyclization, **19**⟶**20**, and the hydrogen shift, **20**⟶**22**, must proceed with $k \geq 10^9\ s^{-1}$. The rate estimated for the first step is consistent with competitive cyclization and quenching of **19** in methanol. The rapid hydrogen shift of **20**, on the other hand, seems surprising in view of the slow conversion of **26** into **27** ($k = 3{\cdot}1\ s^{-1}$ at 23·4 °C).[20] However, *two* benzene rings are regenerated in the isomerization of **20** into **22** ($\Delta H_r \approx 60$ kcal mol^{-1}), compared with one in the **26**⟶**27** transformation ($\Delta H_r \approx 26$ kcal mol^{-1}) [heats of formation (ΔH_f°) for **20** (129·8 kcal mol^{-1}), **22** (70·0 kcal mol^{-1}), **26** (137·3 kcal mol^{-1}) and **27** (110·9 kcal mol^{-1}) were calculated with a force field (MM2ERW) that takes the interaction of π bonds into account[23]]. The enhanced driving force might account for the rapid reaction of **20**. Hence the intermediacy of **20** remains debatable.*

(2′,4′,6′-Trimethylbiphenyl-2-yl)phenylcarbene (30)

The major intramolecular reaction of **30** is insertion into C—H bonds of the *ortho* methyl groups, leading to the dihydrophenanthrene **35**. Photolysis of the diazo compound **29** afforded the methyl ether **34** and **35** in a 15 : 1 ratio, i.e. the cyclization of **30**, with formation of a six-membered ring, is less efficient than that of **19**. Small amounts of the ketone **28** were observed in all photolyses of **29**. In acetonitrile, **35** was also accompanied by 3% of 9-phenyl-4,6,9-trimethylfluorene (**36**). More of the fluorene was obtained in thermolyses of **29**, increasing temperature enhancing the fraction of **36** (Scheme 4). The structure of **36** was confirmed by an unequivocal synthesis, via acid-catalysed ring closure of **32**.

Formally, **30** is converted into **36** by insertion into an Ar—CH_3 bond. Direct insertion into C—C bonds is without precedent even for the most reactive carbenes. Sigmatropic alkyl shifts, on the other hand, are known. Thus, 2,2-dialkyl-2*H*-indenes (**37**) rearrange to give 1,2-dialkyl-1*H*-indenes (**38**) at moderate temperatures (≤ 100 °C).[24a,c] We feel, therefore, that the formation of **36** provides good evidence for the intervention of **31** from which **36** arises by thermal activation.

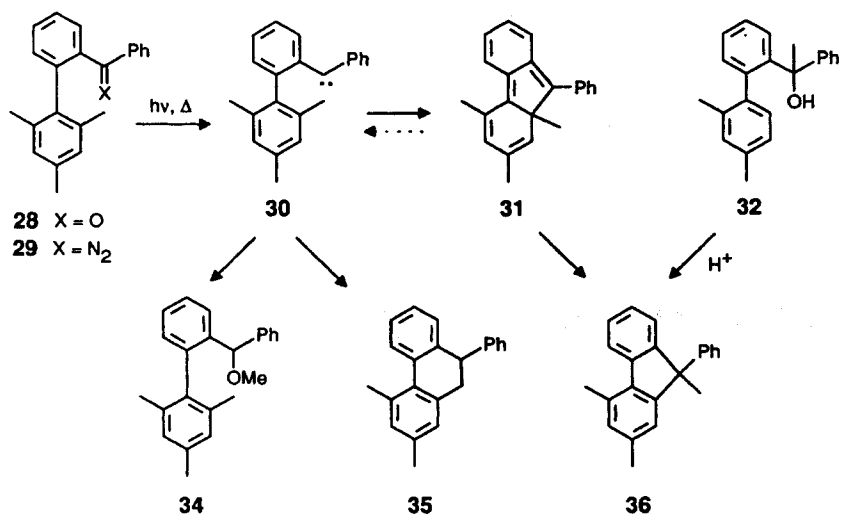


37 **38**

Comparison of carbenes with carbocations

Diarylcarbenium ions have been thoroughly studied by time-resolved spectroscopy. LFP of Ar_2CHX leads to competitive heterolysis ($\rightarrow Ar_2CH^+$) and homolysis ($\rightarrow Ar_2CH\cdot$) of the C—X bond.[25] Alternatively, proton transfer to photogenerated diarylcarbenes gives rise to diarylcarbenium ions ($Ar_2C: + ROH \longrightarrow Ar_2CH^+ RO^-$).[26] Both methods are applicable to biphenylyl precursors. Thus, transient absorption spectra of the

* Direct formation of **22** from the excited diazo compound **18*** was considered by a reviewer. Although carbenic hydrogen shifts can be 'mimicked' by carbene precursors,[15] there is no analogous precedent for cyclizations. As a rule, the product distributions of 'carbene mimics' respond strongly to the mode of excitation (direct or sensitized). In the case of **18**, no significant effect of benzophenone sensitization was observed (Scheme 3). Moreover, the competitive formation of **21** and **22** points to the pivotal role of the carbene **19**.

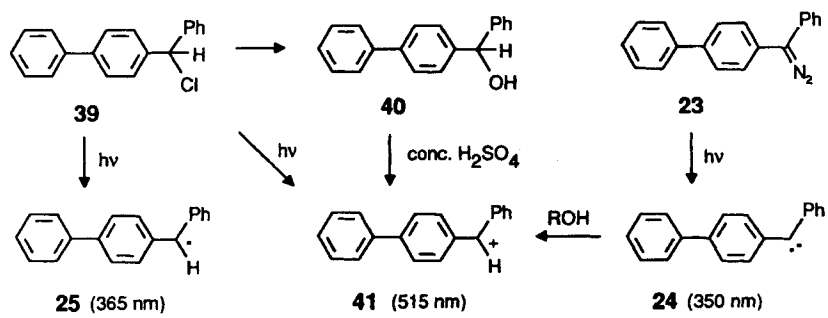


hv, MeOH	88	6	trace
hv, MeCN	–	92	3
Δ, 130°C	–	91	9
Δ, 180-200°C	–	85	15
Δ, 240-260°C	–	82	18

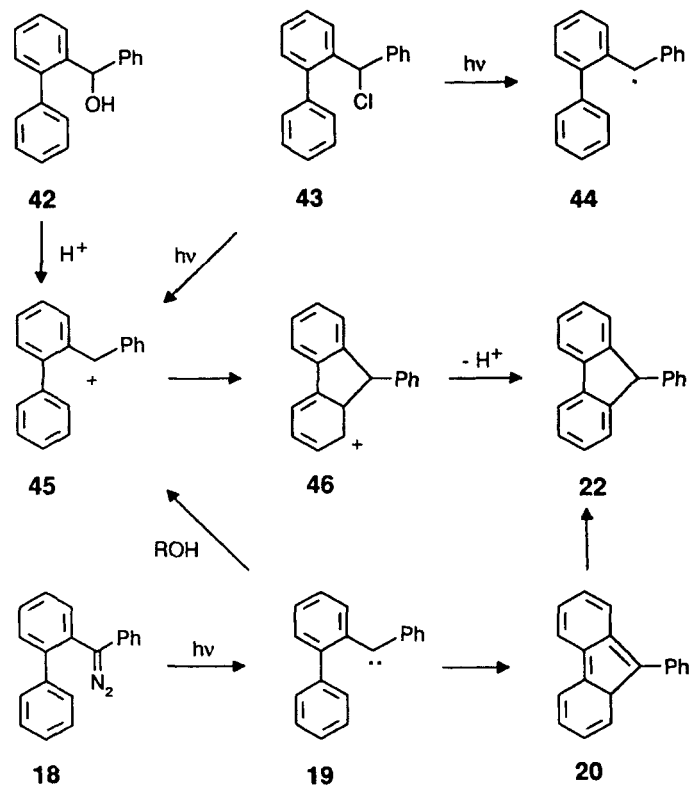
Scheme 4

radical **25** (λ_{max} = 365 nm) and of the cation **41** (λ_{max} = 515 nm) are observed on LFP of the chloride **39** in acetonitrile (AN). LFP of the diazo compound **23** in AN–TFE generates only **41**. Persistent solutions of **41** are obtained when the alcohol **40** is dissolved in concentrated sulphuric acid (Scheme 5).

If **42**, the *ortho* isomer of **40**, is dissolved in concentrated sulphuric acid, a colourless solution results from which 9-phenylfluorene (**22**) can be isolated (Scheme 6). It appears that the carbenium ion **45** undergoes intramolecular Friedel–Crafts alkylation fast enough to escape visual detection. Entirely different results are obtained on the microsecond time-scale. LFP of the chloride **43** generates the cation **45** (λ_{max} = 435, 525 nm) as well as the radical **44** (λ_{max} = 335 nm) (Figure 2). The absorption of **44** is quenched by oxygen whereas that of **45** is quenched by methanol. The transient **45** is also observed on LFP of the diazo precursor **18** in AN–TFE, i.e. proton transfer to the carbene **19** competes with cyclization. The reaction rate of **45** with AN–TFE is nearly the same as that of the *para* isomer **41** (Table 1). Obviously, ring closure, **45**→**46**→**22**, does not contribute significantly to the decay of **45** in AN–TFE. We conclude that cyclization of the carbo-

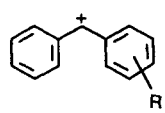


Scheme 5



Scheme 6

Table 1. Spectroscopic and kinetic data for biphenylylcarbenium ions



	Educt	Solvent	λ_{max} (nm)	k_{obs} (s^{-1})[a]
R = H	Chloride[b]	AN[c]	435	2.5×10^6
	Diazo[d]	AN–TFE (1 : 1·6)	430	6.6×10^6
R = 4-Ph (**41**)	Chloride	AN	515	9.1×10^5
	Diazo	AN–TFE (1 : 1·6)	515	9.3×10^5
	Diazo	AN–TFE (1 : 9)	515	4.3×10^5
R = 2-Ph (**45**)	Chloride	AN	435, 525 (~4 : 1)	9.6×10^5
	Diazo	AN–TFE (1 : 1·6)	435, 525 (~4 : 1)	9.2×10^5
	Diazo	AN–TFE (1 : 9)	435, 525 (~4 : 1)	6.3×10^5
R = 2-(*o*-tolyl)	Chloride	AN	440, 525 (~10 : 1)	1.1×10^6
	Diazo	AN–TFE (1 : 9)	440, 525 (~10 : 1)	1.6×10^6
R = 2-mesityl	Chloride	AN	445	1.6×10^6
	Diazo	AN–TFE (1 : 9)	445	1.2×10^6

[a] The precision of rate constants is ~5% and the reproducibility is ~10%.
[b] Ref. 25c.
[c] AN = acetonitrile.
[d] Ref. 26a.

cation **45** ($k \leqslant 10^5\ s^{-1}$) proceeds more slowly than that of the analogous carbene **19** ($k \geqslant 10^9\ s^{-1}$) by a factor of $\geqslant 10^4$. The faster reaction, **19**⟶**20**, is driven by annihilation of the carbenic site whereas the σ complex **46** retains the positive charge of **45**.

The absorption spectra of biphenylylcarbenium ions (Table 1) are interesting in their own right. The absorption maximum of **41** shows a bathochromic shift of 85 nm, relative to that of diphenylcarbenium ion. It is generally known that biaryls have twisted ground state structures with a tendency to become planar when electronically excited.[27] Hence the extended conjugation in **41** stabilizes the S_1 excited state more than the ground state, thus narrowing the energy gap. The absorption spectra of **45** display two maxima at 435 and 525 nm, with an intensity ratio of *ca* 4 : 1. The rates of decay of both bands agree within experimental error, i.e. the same ground state of **45** is involved. We suggest that the 435 nm absorption is due to a transition between twisted S_0 and S_1 states of **45**. This absorption maximum is positioned similar to that of diphenylcarbenium ion since neither state of **45** is stabilized by the extra phenyl group. Excitation from a twisted S_0 to a planar S_1 state creates the 525 nm absorption of **45** which is analogous to that of **41**. The effect of additional *ortho* substituents supports this interpretation. The absorption at 525 nm is attenuated by one 2′-methyl group and disappears on introduction of two 2′-methyl groups (Table 1), as a planar conformation of the excited state is less readily attained.

CONCLUSIONS

The cyclization reactions of biphenyl-2-ylcarbenes, leading to fluorenes, have been identified as rapid processes, with rates of the order of $10^{11}\ s^{-1}$. Unlike intermolecular addition reactions of arylcarbenes with arenes, the intramolecular reactivity of biphenyl-2-ylcarbenes is not significantly affected by substitution at the divalent carbon (R = H, Me, Ph). The presence of two 2′-methyl groups in **30** diverts the carbene to formal C—H insertion, giving the dihydrophenanthrene **35**. Formation of the fluorene **36**, by formal insertion into a C—C bond, occurs as a minor process, particularly on thermal generation of the carbene **30**. This unprecedented reaction points to intervention of the *o*-xylylene **31** although direct observation of *o*-xylylene intermediates has not been achieved. Minor effects of triplet sensitization and methanol quenching indicate that fluorenes arise from spin-equilibrated biphenyl-2-ylcarbenes, presumably from the singlet state.

On LFP of biphenyl-2yldiazomethanes in protic media, proton transfer to biphenyl-2-ylcarbenes occurs competitively with cyclization. The absorption spectra of biphenyl-2-ylcarbenium ions are strongly influenced by the degree of twisting about the Ar—Ar bond whereas the rates of nucleophilic capture are not. Biphenyl-2-ylcarbenium ions cyclize more slowly than the analogous carbenes, by a factor of $\geqslant 10^4$. The enhanced reactivity of the carbene can be attributed to participation of the in-plane σ-orbital which is not available to the carbocation.

EXPERIMENTAL

General. Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. ^{1}H NMR spectra were obtained at 80 MHz (Bruker WP-80) and 400 MHz (Bruker AM-400). ^{2}H (61·42 MHz) and ^{13}C (100·61 MHz) spectra were recorded on a Bruker AM-400 and ^{19}F (75·4 MHz) spectra on a Bruker WP-80 spectrometer. Chemical shifts in $CDCl_3$ are reported in δ (ppm) relative to tetramethylsilane as an internal standard, unless indicated otherwise. Mass spectra (70 eV) were obtained on a Varian-MAT CH5 instrument and IR spectra on a Perkin-Elmer Model 881 spectrometer. GC was performed by the use of a Siemens Sichromat system equipped with glass capillary columns. HPLC was carried out with LDC (Milton Roy) chromatographs with refractometric or UV detection. The equipment and procedure used for laser flash photolysis has been described.[28] Solutions of the substrates were adjusted to an OD at 248 nm of *ca* 1. Photolyses were carried out with *ca* 20 ns pulses of 248 nm light (KrF) from a Lambda Physik EMG 103 MSC excimer laser.

*Photolysis of 2-diazomethyl-1,1′-biphenyl (**1**).* A solution of **1**[7] (194 mg, 1 mmol) in cyclohexane (10 ml), purged with argon, was irradiated (medium-pressure mercury lamp, Pyrex vessel, 20 °C) for 2 h. The solution was concentrated *in vacuo* and the residue (141 mg) was analysed by GC (6·6 m OV-1 column, 120 °C). Apart from small amounts of biphenyl-2-carbaldehyde,[7] fluorene (**3**) and 2-(cyclohexylmethyl)biphenyl[29] (**4**, R = C_6H_{11}) were observed in a 19 : 1 ratio. The hydrocarbons were separated by HPLC [Polygosil 60-5-NO_2 column, pentane–diethyl ether (98 : 2) as eluent] to obtain the spectra of **4** (R = C_6H_{11}). MS (70 eV), *m/z* 250 (57), 178 (5), 168 (100), 152 (15), 115 (5), 83 (20), 55 (38). ^{1}H NMR ($CDCl_3$), δ 0·5–1·7 (m, 11 H), 2·50 (d, J = 6·8 Hz, 2 H), 7·15–7·45 (m, 9 H). ^{13}C NMR ($CDCl_3$), δ 26·30 (C-3″, C-5″), 26·48 (C-4″), 33·11 (C-2″, C-6″), 39·37 (C-1″), 46·60 (α-C), 125·44 (C-5), 126·58 (C-3 or C-6), 126·97 (C-3 or C-6), 127·88 (C-2′, C-6′), 129·43 (C-3′, C-5′), 129·93 (C-4 or C-4′), 129·99 (C-4 or C-4′), 138·82 (C-2), 141·29 (C-1 or C-1′), 142·39 (C—1 or C-1′).

For an alternative approach to **4** (R = C_6H_{11}), cyclohexylmagnesium bromide was added to biphenyl-2-carbaldehyde[7] in diethyl ether to give 52% of α-cyclohexylbiphenyl-2-methanol. ^{1}H NMR ($CDCl_3$), δ

0·5–2·1 (m, 12 H), 4·46 (d, J = 7·8 Hz, 1 H), 7·1–7·6 (m, 9 H). Hydrogenation (10% Pd–C, ethyl actetate, 400 kPa, 20 °C, 48 h) of the carbinol provided 89% of 2-(cyclohexylmethyl)biphenyl, identical in every respect with the product obtained from **1**.

1-(Biphenyl-2-yl)ethanone p-toluenesulphonylhydrazone (7) and sodium salt (8). 1-(Biphenyl-2-yl)ethanone (**14**), m.p. 56 °C,[30] was prepared in 96% yield by reacting biphenyl-2-carboxylic acid (Aldrich) with methyllithium, according to a standard procedure.[31] To a solution of **14** (3·0 g, 15·3 mmol) in methanol (20 ml) was added a solution of *p*-toluenesulphonylhydrazine (2·86 g, 15·3 mmol) in methanol (15 ml). The mixture was stirred for 10 min and then cooled to 0 °C. A crystalline precipitate formed slowly which, after 16 h, was filtered off and recrystallized from methanol to give 2·47 g (44%) of **7**; m.p. 163 °C. ^{1}H NMR ($CDCl_3$), δ 1·45 (s, 3 H), 2·46 (s, 3 H), 7·05–7·45 (m, 12 H), 7·89 (d, J = 8 Hz, 2 H). Analysis: calculated for $C_{21}H_{21}N_2O_2S$, C 69·01, H 5·79, N 7·66; found, C 69·02, H 5·75, N 7·66%.

To a solution of **7** (1·2 g, 3·3 mmol) in anhydrous THF (10 ml) was added sodium hydride (55% dispersion in mineral oil, 145 mg, 3·3 mmol). With exclusion of moisture, light and oxygen, the mixture was stirred for 30 min at room temperature. *n*-Pentane (30 ml) was then added and stirring was continued for 30 min. The precipitate was filtered with suction, washed with *n*-pentane and dried *in vacuo* to give 1·06 g (83%) of the sodium salt **8**.

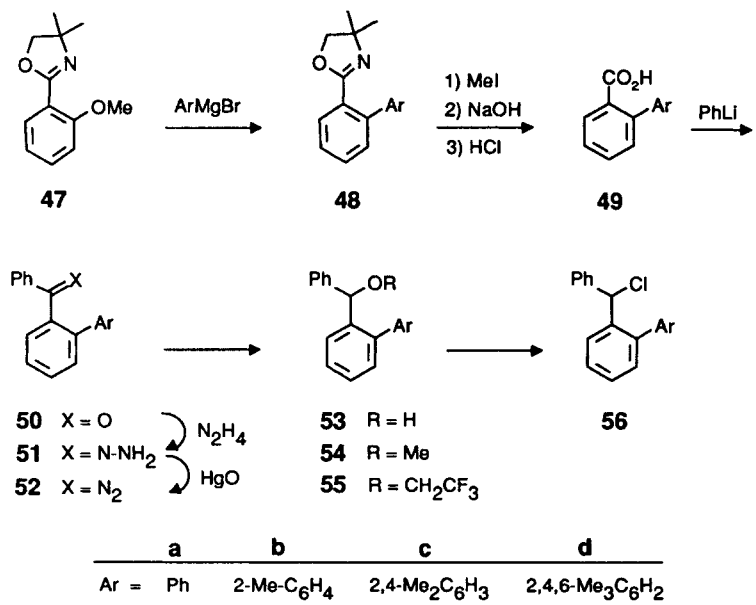
Thermolysis and photolysis of 8. The apparatus used for the flash vacuum pyrolysis of tosylhydrazone sodium salts has been described.[32] Compound **8** (100 mg, 0·26 mmol) was thermolysed at 300 °C/0·01 Torr (1 Torr = 133·3 Pa); the products were collected in a trap cooled with liquid nitrogen. After having been warmed to 20 °C, the product mixture was dissolved in diethyl ether and analysed by GC (24·5 m OV-1 column, 140 °C). 2-Ethenylbiphenyl (**11**, 12·9%)[30,33] and 9-methylfluorene (**13**, 87·1%)[34] were identified by comparison with authentic samples. The combined yield was estimated as 67%, using fluorene as an internal standard.

A solution of **7** (100 mg, 0·27 mmol) in 0·2 M NaOMe–MeOH (10 ml) was purged with nitrogen and photolysed (medium-pressure mercury lamp, Pyrex vessel, 20 °C) for 90 min. Diethyl ether (60 ml) was added and the mixture was washed three times with a saturated aqueous solution of NaCl. The organic phase was dried ($MgSO_4$), concentrated *in vacuo*, and analysed by GC (24·5 m OV-1 column, 140 °C). In addition to the major products **12** and **13**, traces ($\leq$0·2%) of **11** and **14** and 1·9% of 2-ethylbiphenyl[35] were detected (Scheme 2). A combined yield of 44% was estimated (GC). 2-(1-Methoxyethyl)biphenyl (**12**) and 9-methylfluorene (**13**) were isolated by HPLC [Polygosil 60-6 column, *n*-pentane–diethyl ether (80 : 1) as eluent]. The ether **12** was also prepared by reduction of **14** with $LiAlH_4$ (86%), followed by methylation of 1-(biphenyl-2-yl)ethanol, m.p. 111 °C,[30] with MeI–NaH (91%). 1 H NMR ($CDCl_3$), δ 1·27 (d, J = 6·4 Hz, 3 H), 3·04 (s, 3 H), 4·32 (q, J = 6·4 Hz, 1 H), 7·0–7·6 (m, 9 H). Analysis: calculated for $C_{15}H_{16}O$, C 84·87, H 7·60; found, C 84·81, H 7·53%.

Photolysis of 2-(1-diazoethyl)biphenyl (9). To a solution of **7** (250 mg, 0·68 mmol) in 1,4-dioxane (10 ml) was added 50% aqueous NaOH (1 ml). With exclusion of light and oxygen, the mixture was stirred at 80 °C for 1 h, cooled to 20 °C and extracted with *n*-pentane. The extracts were washed with water, dried ($MgSO_4$) and concentrated under reduced pressure to give 107 mg (75%) of crude **9**. IR ($CDCl_3$), 2010 cm^{-1}. ^{1}H NMR ($CDCl_3$), δ 1·88 (s, 3 H), 7·0–7·6 (m, 9 H). A solution of **9** (15 mg, 0·07 mmol) in benzene (2 ml) was photolysed as described above, yielding the product mixture (89%) recorded in Scheme 2. For triplet sensitization, benzophenone (150 mg, 0·8 mmol) was added to the benzene solution of **9**.

2-Arylbenzophenones (50) and related compounds. Biphenyl-2-carboxylic acid (**49a**) is commercially available (Aldrich). A solution of 2-iodobenzoic acid in C_6D_6 was irradiated, as described for C_6H_6,[35] in order to obtain **49a**-d_5. The oxazoline route developed by Meyers *et al.*[36] was applied to prepare the acids **49b–d** (Scheme 7). 2-(2-Methoxyphenyl)-4,4-dimethyl-2-oxazoline (**47**) was treated with the appropriate Grignard reagent to give the oxazolines **48b** [80%; ^{1}H NMR ($CDCl_3$), δ 1·18 (s, 6 H), 2·10 (s, 3 H), 3·66 (s, 2 H), 7·1–7·5 (m, 7 H), 7·7–7·9 (m, 1 H)], **48c** [88%; ^{1}H NMR ($CDCl_3$), δ 1·18 (s, 6 H), 2·07 (s, 3 H), 2·34 (s, 3H), 3·67 (s,2H), 6·98 (s,3H), 7·1–7·8 (m, 4H)] and **48d** [64%; ^{1}H NMR ($CDCl_3$), δ 1·14 (s, 6 H), 1·93 (s, 6 H), 2·30 (s, 3 H), 3·64 (s, 2 H), 6·83 (s, 2 H), 7·0–7·8 (m, 4 H)]. Methylation and hydrolysis[36] of **48** afforded the acids **49**: 2′-methylbiphenyl-2-carboxylic acid (**49b**)[37] [55%; m.p. 103–104 °C; ^{1}H NMR ($CDCl_3$), δ 2·03 (s, 3 H), 7·0–7·65 (m, 7 H), 7·95–8·1 (m, 1 H), 8·9 (br. s, 1 H)]; 2′,4′-dimethylbiphenyl-2-carboxylic acid (**49c**) [75%; m.p. 126–127 °C; ^{1}H NMR ($CDCl_3$), δ 2·03 (s, 3 H), 2·37 (s, 3 H), 7·03 (m, 3 H), 7·15–7·65 (m, 3 H), 7·95–8·1 (m, 1 H)]; 2′,4′,6′-trimethylbiphenyl-2-carboxylic acid (**49c**) [84%; m.p. 172–173 °C; ^{1}H NMR ($CDCl_3$), δ 1·89 (s, 6 H), 2·31 (s, 3 H), 6·88 (s, 2 H), 7·05–7·75 (m, 3 H), 8·0–8·15 (m, 1 H)].

2-Arylbenzophenones (**50**) were obtained by reaction of **49** with phenyllithium, using standard procedures.[31,38] (Biphenyl-2-yl)phenylmethanone (**50a**):[39] 62%; m.p. 91–92 °C. IR (KBr), 1662 cm^{-1} (C=O). (2′-Methylbiphenyl-2-yl)phenylmethanone (**50b**): 44%; oil.



Scheme 7

IR (CCl_4), 1665 cm^{-1} (C=O); ^1H NMR ($CDCl_3$), δ 2·15 (s, 3 H), 6·95–7·7 (m, 13 H). (2′,4′-Dimethylbiphenyl-2-yl)phenylmethanone (**50c**): 37%; m.p. 59–61 °C. IR (CCl_4), 1670 cm^{-1} (C=O); ^1H NMR ($CDCl_3$), δ 2·09 (s,3H), 2·21 (s, 3 H), 6·87 (m, 3 H), 7·1–7·7 (m, 9 H). (2′,4′,6′-Trimethylbiphenyl-2-yl)phenylmethanone (**50d** = **28**): 60%; m.p. 136–137 °C. IR (KBr), 1660 cm^{-1} (C=O); ^1H NMR ($CDCl_3$), δ 1·94 (s, 6 H), 2·23 (s, 3 H), 6·78 (s, 2 H), 7·15–7·75 (m, 9 H).

In order to prepare the hydrazones **51**, solutions of 2-arylbenzophenones (10 mmol) and hydrazine hydrate (0·1 mol) in butan-1-ol (15 ml) were heated at 110–120 °C.[40] Long reaction times (specified below) were required, owing to steric hindrance. The reaction mixtures were concentrated *in vacuo*. On trituration of the residue with diethyl ether–hexane at −20 °C, crystals of **51a** were obtained. Compounds **51b** and **d** did not crystallize at this stage and were purified by low-pressure (LP) LC [silica gel, diethyl ether–hexane (1 : 1) as eluent]. (Biphenyl-2-yl)phenylmethanone hydrazone (**51a**): 20 h, 66%, m.p. 85–86 °C. IR (KBr), 1585 cm^{-1} (C=N); ^1H NMR ($CDCl_3$), δ 7·05–7·6 (m). Analysis: calculated for $C_{19}H_{16}N_2$, C 83·79, H 5·92, N 10·28; found, C 83·72, H 5·83, N 10·28%. (2′-Methylbiphenyl-2-yl)phenylmethanone hydrazone (**51b**): 30 h, 48%, m.p. 103–105 °C; IR (KBr), 1580 cm^{-1} (C=N); ^1H NMR ($CDCl_3$), δ 2·02 (s, 3 H), 5·47 (br s, 2H), 7·02 (br s, 4 H), 7·14 (br s, 5 H), 7·4–7·7 (m, 4 H). (2′,4′,6′-Trimethylbiphenyl-2-yl)phenylmethanone hydrazone (**51d**): 4·5 days, 44%, m.p. 105–107 °C; LPLC afforded two isomers (A and B, 1 : 1) whose mass spectra and IR spectra agreed closely whereas the NMR spectra were different: MS (70 eV), *m/z* 314 (M^+, 22%), 299 (49%), 283 (100%), 268 (40%), 253 (11%); IR ($CDCl_3$), 1605 cm^{-1} (C=N); ^1H NMR ($CDCl_3$), (A) δ 1·47 (s, 3 H), 2·03 (s, 3 H), 2·17 (s, 3 H), 5·54 (s, 2 H), 6·42 (s, 2 H), 6·81 (s, 1 H), 6·95–7·6 (m, 9 H), (B) 1·66 (s, 6 H), 2·23 (s, 3 H), 5·37 (br. s, 2 H), 6·6–6·75 (m, 3 H), 6·95–7·7 (m, 8 H). The spectrum of A shows non-equivalence of the *o*′-methyl groups and *m*′-hydrogens. Coalescence of these signals at *ca* 60 °C points to restricted rotation, which is most likely for *syn*-**51d**. GC at 175 °C (8 m OV-17 column) led to partial interconversion of A and B.

Solutions of the hydrazones **51** (4 mmol) in diethyl ether (50 ml) were oxidized with HgO (3 × 20 mmol) in the presence of Na_2SO_4 (3 × 40 mmol) and 30% ethanolic KOH (3 × 10 drops).[41] The reagents were added in three portions, after 0, 2 and 4 h, while the mixture was vigorously agitated at 20 °C. Stirring was continued in the dark for 24–48 h, until the GC peak of **51** had disappeared. The solution was then filtered and concentrated *in vacuo* at 20 °C. The diazo compounds **52** were recrystallized from pentane at −30 °C but were liquids at room temperature. (Biphenyl-2-yl)phenyldiazomethane (**18** = **52a**): 97%. IR (film), 2046 cm^{-1} (C=N_2); UV (MeCN), 227 (ε = 20 330), 289 nm (ε = 18 190); ^1H NMR (CD_3COCD_3), δ 6·9–7·65 (m). (2′-Methylbiphenyl-2-yl)phenyldiazomethane (**52b**): 50%. IR ($CDCl_3$), 2048 cm^{-1} (C=N_2); UV (MeCN), 289 nm (ε = 20 000); ^1H NMR ($CDCl_3$), δ 2·1 (s, 3 H), 6·9–7·6 (m, 13 H). (2′,4′,6′-Trimethylbiphenyl-2-yl)phenyldiazomethane

(**29** = **52d**): 58%. IR (film), 2043 cm^{-1} (C=N_2); UV (MeCN), 291 nm (ε = 18 870); ^1H NMR ($CDCl_3$), δ 1·98 (s, 6 H), 2·32 (s, 3 H), 6·85–7·65 (m, 11 H).

The carbinols **53** were obtained by reduction of **50** with $LiAlH_4$ in diethyl ether. (Biphenyl-2-yl)phenylmethanol (**53a**):[42] 82%, m.p. 69 °C. ^1H NMR ($CDCl_3$), δ 2·55 (d, J = 4 Hz, 1 H), 5·95 (d, J = 4 Hz, 1 H), 7·1–7·7 (m, 14 H). (2′-Methylbiphenyl-2-yl)phenylmethanol (**53b**): 79%, oil. ^1H NMR ($CDCl_3$), δ 1·58 (d, J = 4·5 Hz, 0·45 H), 1·63 (s, 1·35 H), 2·07 (d, J = 3·5 Hz, 0·55 H), 2·17 (s, 1·65 H), 5·59 (d, J = 4·5 Hz, 0·45 H), 5·62 (d, J = 3·5 Hz, 0·55 H), 6·8–7·8 (m, 13 H). This NMR spectrum indicates the presence of diastereomers, resulting from two elements of chirality (centre and axis). (2′,4′,6′-Trimethylbiphenyl-2-yl)phenylmethanol (**53d**): 92%. ^1H NMR ($CDCl_3$), δ 1·45 (s, 3 H), 2·07 (s, 3 H), 2·15 (br. s, 1 H), 2·38 (s, 3 H), 5·46 (s, 1 H), 6·8–7·8 (m, 11 H).

To a suspension of PCl_5 (0·40 g, 2 mmol) in anhydrous diethyl ether (20 ml) was added a solution of **53** (1 mmol) in diethyl ether (2 ml). The mixture was heated at reflux for 2 h and then hydrolysed by dropwise addition of water. The phases were separated; the aqueous phase was saturated with NaCl and extracted with diethyl ether. The combined ether solutions were dried ($MgSO_4$) and evaporated under reduced pressure to give the chlorides **56**. 2-(α-Chlorophenylmethyl)biphenyl (**43** = **56a**):[42] 60%. ^1H NMR ($CDCl_3$), δ 6·32 (s, 1 H), 7·3–7·5 (m, 13 H), 7·7–7·8 (m, 1 H). 2-(α-Chlorophenylmethyl)-2′-methylbiphenyl (**56b**): 56%. ^1H NMR ($CDCl_3$), δ 1·68 and 2·17 (2s, 3 H), 5·86 and 5·95 (2s, 1 H), 6·8–7·8 (m, 13 H). 2-(α-Chlorophenylmethyl)-2′,4′,6′-trimethylbiphenyl (**56d**): 70%. ^1H NMR ($CDCl_3$): δ 1·50 (s, 3 H), 2·10 (s, 3 H), 2·37 (s, 3 H), 5·79 (s, 1 H), 6·8–8·0 (s, 11 H).

Photolyses of (biphenyl-2-yl)phenyidiazomethanes (52). Degassed solutions of **52** (0·01 M) in acetonitrile, methanol and AN–TFE were irradiated (20 °C, Pyrex vessels) with a medium-pressure mercury lamp (150 W) for 15–30 min. The products were analysed by GC (OV-1 column, 160–200 °C) and isolated by HPLC [Polygosil 60-5-NO_2 column, pentane–diethyl ether (1 : 1) as eluent]. Diazo compound **18** (=**52a**) afforded 2-(α-methoxyphenylmethyl)biphenyl (**21**-OMe = **54a**)[42] [^1H NMR ($CDCl_3$), δ 3·22 (s, 3 H), 5·31 (s, 1 H), 7·1–7·7 (m, 14 H)], the analogous 2,2,2-trifluoroethyl ether (**21**-OCH_2CF_3 = **55a**) [^1H NMR ($CDCl_3$), δ 3·61 (q, J = 9 Hz, 2 H), 5·58 (s, 1 H), 7·1–7·75 (m, 14 H); ^{19}F NMR ($CDCl_3$), δ −75·06 (t, J = 9 Hz)] and 9-phenylfluorene (**22**)[43] [^1H NMR ($CDCl_3$), δ 5·05 (s, 1 H), 7·0–7·5 (m, 11 H), 7·7–7·9 (m, 2 H)]. For product distributions, see Scheme 3.

Photolysis of **52b** in acetonitrile gave 4-methyl-9-phenylfluorene [92%; ^1H NMR ($CDCl_3$), δ 2·80 (s, 3 H), 5·05 (s, 1 H), 7·0–7·55 (m, 11 H), 7·9–8·05 (m, 1 H)] and **50b** (7%). In methanol, we obtained 2-(α-methoxyphenylmethyl)-2′-methylbiphenyl (**54b**) [84%; ^1H NMR ($CDCl_3$), δ 1·58 and 2·18 (2s, 3 H), 3·24 and 3·26 (2s, 3 H), 5·02 and 5·16 (2s, 1 H), 6·8–7·8 (m, 13 H)], 4-methyl-9-phenylfluorene (10%) and **50b** (6%). Photolysis of **52b** in AN–TFE (1 : 9) afforded **55b** [80%; ^1H NMR ($CDCl_3$), δ 1·52 and 2·12 (2s, 3 H), 3·4–3·8 (m, 2 H), 5·23 and 5·36 (2s, 1 H), 6·8–7·8 (m, 13 H)], 4-methyl-9-phenylfluorene (17%) and **50b** (3%).

The major product obtained by photolysis of **29** (=**52d**) in methanol was 2-(α-methoxyphenylmethyl)-2′,4′,6′-trimethylbiphenyl (**34** = **54d**). ^1H NMR ($CDCl_3$), δ 1·39 (s, 3 H), 2·11 (s, 3 H), 2·30 (s, 3 H), 3·27 (s, 3 H), 4·88 (s, 1 H), 6·8–7·85 (m, 11 H). Photolysis of **29** in acetonitrile gave predominantly 9,10-dihydro-2,4-dimethyl-9-phenylphenanthrene (**35**): m.p. 104–105 °C; ^1H NMR ($CDCl_3$), δ 2·30 (s, 3 H), 2·63 (s, 3 H), 3·00 (dd, J = 14·5, 4·5 Hz, 1 H), 3·15 (dd, J = 14·5, 10·5 Hz, 1 H), 4·03 (dd, J = 10·5, 4·5 Hz, 1 H), 6·87 (m, 2 H), 7·00 (s, 1 H), 7·15–7·35 (m, 7 H), 7·70 (dd, J = 7·8, 0·9 Hz, 1 H). See Scheme 4 for product distributions. 2,4,9-Trimethyl-9-phenylfluorene (**36**) was obtained, along with **35**, by thermolysis of **29** in chlorobenzene [0·02 M, 130 °C, 15 min; HPLC on Polygosil 60-5-C_{18} column, methanol–water (8 : 2) as eluent]. The spectra of **36** were in excellent agreement with those of an authentic sample (see below). For pyrolyses at higher temperatures, **29** was decomposed in the inlet of a gas chromatograph (column temperature 170 °C, 6·6 m OV-1 column). Photolysis of **29** in AN–TFE (1 : 9) afforded 98% of **55d** [^1H NMR ($CDCl_3$), δ 1·33 (s, 3H), 2·05 (s, 3 H), 2·36 (s, 3 H), 3·58 (m, 2 H), 5·1 (s, 1 H), 6·8–7·8 (m, 11 H); ^{19}F NMR ($CDCl_3$), δ −75·01 (t, J = 9 Hz)] and 2% of **28** (=**50d**); **35** and **36** were not detected.

2,4,9-Trimethyl-9-phenylfluorene (36). To a solution of **50c** (2·0 g, 7·0 mmol) in anhydrous diethyl ether (20 ml) was added at 0 °C ethereal methyllithium (1·6 M, 4·4 ml, 7·04 mmol). After having been stirred at 0 °C for 3 h, the mixture was partitioned between water and diethyl ether. The combined ether solutions were dried ($MgSO_4$) and evaporated under reduced pressure. LPLC [silica gel, pentane–diethyl ether (97 : 3) as eluent] of the residue afforded two fractions (diastereomers?) of 1-(2′,4′-dimethylbiphenyl-2-yl)-1-phenylethanol (**32**) (1·0 and 0·8 g, 85%) which showed nearly the same, very complex ^1H NMR ($CDCl_3$) spectra, presumably due to equilibration.

The alcohol **32** (50 mg, 0·17 mmol) was treated with a 10% solution of H_2SO_4 in acetic acid (2 ml). After 3 h at room temperature, the mixture was neutralized with aqueous $NaHCO_3$ and extracted with diethyl ether. The combined extracts were washed with water, dried ($MgSO_4$), and evaporated under reduced pressure. The

residue was purified by HPLC [Polygosil 100-5 column, pentane–diethyl ether (97 : 3) as eluent] to give 40 mg (81%) of **36**, m.p. 110–111 °C. ^{1}H NMR ($CDCl_3$), δ 1·87 (s, 3 H), 2·32 (s, 3 H), 2·73 (s, 3 H), 6·90 (s, 1 H), 6·97 (s, 1 H), 7·15–7·3 (m, 7 H), 7·36 (m, 2 H), 7·88 (d, J = 8 Hz, 1 H); ^{13}C NMR ($CDCl_3$), δ 20·89 (CH_3), 21·40 (CH_3), 25·53 (CH_3), 54·12 (C), 122·24 (CH), 122·74 (CH), 123·99 (CH), 126·17 (CH), 126·50 (CH), 126·58 (CH), 126·99 (CH), 128·21 (CH), 130·41 (CH), 132·81 (C), 135·10 (C), 137·21 (C), 140·82 (C), 145·50 (C), 154·31 (C), 154·68 (C). Analysis: calculated for $C_{22}H_{20}$, C 92·91, H 7·09; found, C 92·81, H 7·05%.

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