The One-electron Oxidation of Biphenyl-2-ylethylenes. Subsequent Chemical Reactivity Controlled by Electron Return or Proton Transfer

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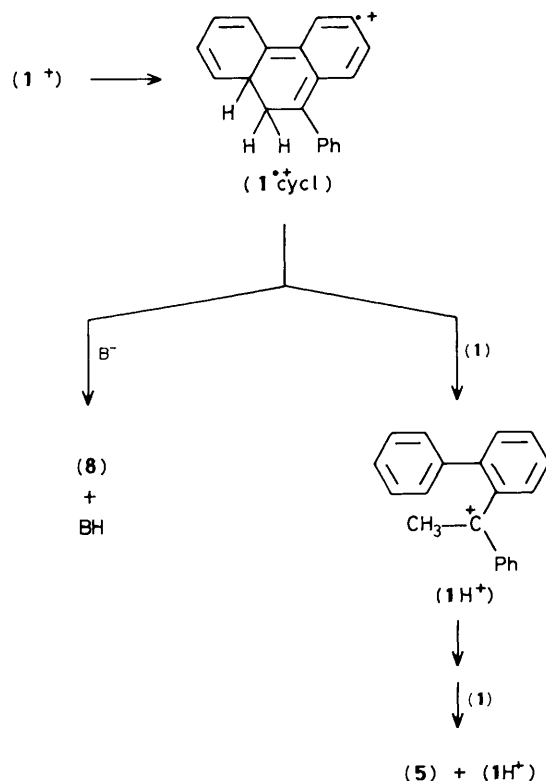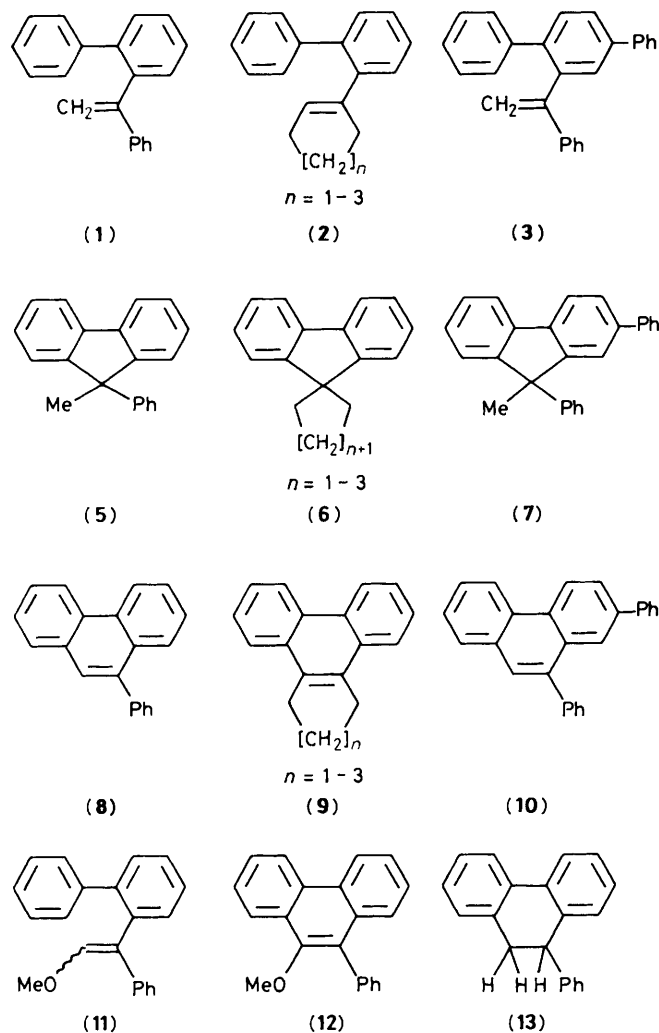[b] Ecole Nationale Supérieure de Chimie et de Physique de Bordeaux, 33405, Talence Cedex, France

Biphenyl-2-ylethylenes react with $(4\text{-}BrC_6H_4)_3N^{\cdot+}SbCl_6^-$ to give the radical cation of the electrocyclization product which initiates a protic catalysis to the related fluorenes or, in presence of 2,6-di-t-butylpyridine or water, lead stoicheiometrically to phenanthrenes; with photochemical oxidants only phenanthrenes or 9,10-dihydrophenanthrenes are obtained, with an efficiency related to the polarity of the solvent and the relative energies of the triplet donor and of the radical ion pair.

Catalysis of the Diels–Alder reaction by single-electron acceptors has been shown to provide a powerful and highly selective route for the cycloaddition of neutral or electron-rich dienophiles to conjugated dienes.[1] However, when the electron acceptor is an aminium radical cation, the catalysed Diels–Alder reaction observed is sometimes a protic acid-catalysed process,[2] and when cyano-arenes in the singlet excited states are used, a triplex could be the source of the adducts.[3]

We report here a radical cation six-atom electrocyclization which could be regarded as an internal Diels–Alder reaction. Since the protic acid-catalysed process leads to a different product, we have been able to distinguish easily between the two pathways.

(1)

(2)
$n = 1-3$

(3)

(5)

(6)
$n = 1-3$

(7)

(8)

(9)
$n = 1-3$

(10)

(11)

(12)

(13)

(1$\cdot^+$) $\longrightarrow$

(1$\cdot^+_{cycl}$)

(8)
+
BH

(1H$^+$)

(5) + (1H$^+$)

Scheme 1

Table 1. Effect of solvent and of additives on the quantum yields of products formation $\phi(8)$, $\phi(13)$, and of DCA disappearance ϕ ($-$DCA), from irradiation at 376 nm of 5×10^{-3} M (1) and 5×10^{-4} M DCA.

Additives	Solvent				
	MeCN			CH$_2$Cl$_2$	Benzene
TMB	—	—	5×10^{-2} M	—	—	—
BP	—	5×10^{-2} M	—	—	5×10^{-2} M	—
$\phi(8)$	0.06	0.17	0.00	0.00	0.00	0.00
$\phi(13)$	0.14	0.13	0.00	0.17	0.09	0.00
$\phi(-$DCA)	0.03	0.08	0.00	0.00	0.00	0.00

Treatment of a nitrogen-saturated solution of 1-(biphenyl-2-yl)-1-phenylethylene (1), or the related compounds (2) or (3), in CH$_2$Cl$_2$, at room temperature, with 10 mol% tris-(4-bromophenyl)aminium hexachloroantimonate (4$\cdot^+$), resulted, respectively, in the formation of the related fluorene derivatives (5)—(7) (60—95%) accompanied, respectively, by trace amounts of the phenanthrenes (8)—(10). When 2,6-di-t-butylpyridine (B, 2 equiv.) or water was added, the formation of (5)—(7) was inhibited and (8)—(10) were produced stoicheiometrically. The results are consistent with a stoi-

cheiometric radical cation cyclization to phenanthrenes and a protic acid-catalysed process to fluorenes (Scheme 1).

In Spectrograde acetonitrile we obtained a low yield of phenanthrenes except with (11), where (12) is formed instantaneously and stoicheiometrically at room temperature. The debromodimerization[4] of (4$\cdot^+$) in MeCN could account for the low reactivity of (1)—(3) [(11) is more easily oxidized since E_{ox} (11) = 1.24 V and E_{ox} (1) = 1.64 V vs. standard calomel electrode (s.c.e.) in MeCN]. The higher basicity of MeCN, or of the residual water, as compared with (1)—(3) and (11), explains the inefficient protic acid reaction.

In anhydrous CH$_2$Cl$_2$, with 10 mol% of (4$\cdot^+$), (11) led to (8) (>90%) as a result of protonation of the oxygen. Addition of 2,6-di-t-butylpyridine suppressed the formation of (8), and (12) was formed stoicheiometrically (Scheme 2).
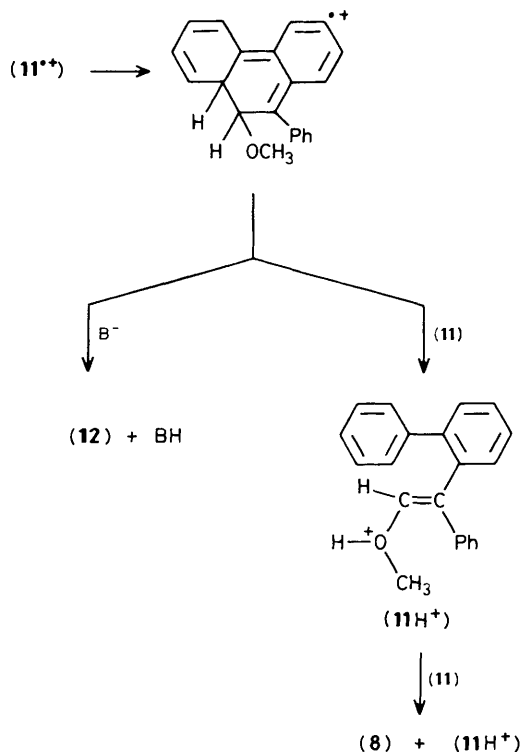
If the protic catalyst were a radical cation, as suggested in Schemes 1 and 2, we could expect to reduce the acid process by using a photochemical oxidant, since after electron exchange, reversible electron transfer would be favoured both by electrostatic attraction within the charged radical ion pair and by simple thermodyanamics. Additionally, the acceptor anion radical should be a good proton trap.

Indeed, irradiation of 9,10-dicyanoanthracene (DCA) (5 × 10^{-4}M) in a nitrogen-saturated acetonitrile solution containing 5 × 10^{-3}M (1) gave both (8) and (13), while DCA disappeared and (5) could not be detected. The same cyclization, leading almost exclusively to (13), was observed with 9-cyanoanthracene (less efficient), 1,4-dicyanonaphthalene, and 9-cyanophenanthrene (more efficient) as excited electron acceptors. With chloranil, only (8) is observed and with 2,4,6-triphenylpyrylium tetrafluoroborate a mixture of (8) and (13) is formed whereas the disappearance of the two sensitizers accompanied the formation of (8).
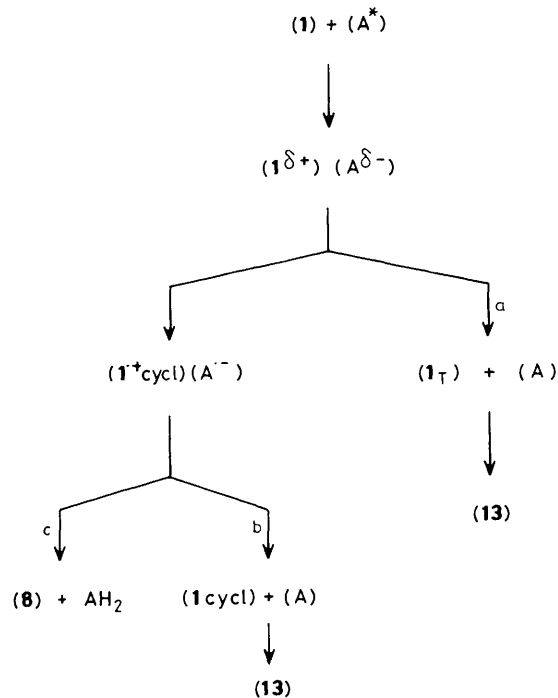
Scheme 2

Scheme 3

The quantum yields for the reaction of (1) (5×10^{-3} M) with excited DCA are shown in Table 1.

An efficient cyclization was observed only in polar or moderately polar solvents. Estimation of the free energy change by the Rehm–Weller equation[5] suggested that the electron transfer process from (1) to the excited singlet state of DCA should be exothermic (ΔG −9.45 kcal mol^{-1} in MeCN; 1 cal = 4.184 J). The quenching of the fluorescence of DCA was indeed almost diffusion-controlled in MeCN (k_q 1.3 $\times$ 10^{10} dm^3 mol^{-1} s^{-1}) whereas an exciplex was observed in CH$_2$Cl$_2$.

The results implicate two distinct mechanisms (Scheme 3).

In MeCN the initial reaction between (1) and the excited singlet state of DCA involves electron transfer to give ($1^{\cdot+}$), (DCA$^{\cdot-}$). The radical cation of the singlet geminate radical ion pair cyclizes to the polyene radical cation ($1^{\cdot+}$ cycl.) which is reduced by DCA$^{\cdot-}$ and leads to (13) (path b) or is deprotonated to (8) and DCAH$_2$ (path c).

The quenching of the reaction in MeCN by 1,2,4-tri-methoxybenzene (TMB) gives evidence for a cationic intermediate but the presence of biphenyl (BP) increases ϕ(8) and ϕ(−DCA) (Table 1). A secondary electron transfer to BP$^{\cdot+}$, already proposed by Schaap for other systems,[6] might explain the increased reactivity and, since this process leads ultimately to the out-of-cage reaction between ($1^{\cdot+}$ cycl.) and (DCA$^{\cdot-}$), the electron return is slower than in the singlet geminate ion pair (multiplicity effect) and the ratio (path c/path b) increases as observed.

In CH$_2$Cl$_2$, only (13) is formed and DCA is not consumed. Since we observed an exciplex and calculated an energy of the radical ion pair[7] (E.i.p. = 62 kcal mol^{-1}) close to the triplet energy of (1) (63 kcal mol^{-1}), we suggest a triplet pathway for the cyclization[8] (path a). The same pathway could be followed in MeCN, when the sensitizers are 1,4-dicyanonaphthalene (DCN) or 9-cyanophenanthrene (CNP) since E.i.p. (DCN$^{\cdot-}$, $1^{\cdot+}$) = 66 kcal mol^{-1}, E.i.p. (CNP$^{\cdot-}$, $1^{\cdot+}$) = 79.7 kcal mol^{-1} and again only (13) is formed.

References

1 D. J. Bellville, D. W. Wirth, and N. L. Bauld, *J. Am. Chem. Soc.*, 1981, **103**, 718.

2 P. G. Gassman and D. A. Singleton, *J. Am. Chem. Soc.*, 1984, **106**, 7993.

3 G. C. Calhoun and G. B. Schuster, *Tetrahedron Lett.*, 1986, **27**, 911.

4 L. Eberson and B. Larsson, *Acta Chem. Scand., Ser. B.*, in the press. We thank Professor Eberson for informing us of this result prior to publication.

5 D. Rehm and A. Weller, *Isr. J. Chem.*, 1970, **8**, 259.

6 A. Schaap, L. Lopez, and S. D. Gagnon, *J. Am. Chem. Soc.*, 1983, **105**, 663.

7 A. Weller, *Z. Phys. Chem. (Frankfurt am Main)*, 1982, **133**, 93.

8 S. Lazare, R. Lapouyade, and R. Bonneau, *J. Am. Chem. Soc.*, 1985, **107**, 6604.