Photocyclization of arylethylenes: Mechanism and scope of the reactions

R LAPOUYADE

Photophysique et Photochimie Moléculaire, UA du CNRS N° 348, Université Bordeaux I, 33405 Talence, France

Abstract. The photocyclization of three structural types of arylethylenes is systematically investigated in order to provide new pathways to regiospecifically substituted and/or partially hydrogenated polycyclic aromatic hydrocarbons. The scope of the photoformation of acenaphthenes from α -arylolefins, in amine solutions, is discussed: when the double bond is acyclic, only the naphthyl and the pyrenyl derivatives are photoreactive, but when the double bond is in a cycle, all the compounds which lead to the *trans* double bond photocyclize. The amine-mediated 1,3-H-shift, discovered with the preceding series, also occurs with 4a,4b-dihydrophenanthrene, formed by irradiation of 1,2-diarylethylenes, and leads to dihydrophenanthrenes. The photocyclization of 2-vinylbiphenyls is stereoselective from the singlet excited state but not from the triplet, where a fast equilibrium between *E* and *Z* configurations precedes the adiabatic cyclization. The radical cation of 2-vinylbiphenyls cyclizes to a phenanthrene radical cation which initiates a protic catalysis to the related fluorenes or, in presence of 2,6-di-*t*-butylpyridine or water, leads stoichiometrically to phenanthrenes.

Keywords. Arylethylenes; photocyclization; amine-mediated proton shift; polycyclic aromatic hydrocarbons.

1. Introduction

Photocyclization of arylethylenes is the preferred method for synthesis of many different polycyclic aromatic hydrocarbons (PAH). There is an overwhelming amount of literature, recently surveyed (Laarhoven 1983; Mallory and Mallory 1984; Liu *et al* 1991), on the photocyclodehydrogenation of 1,2-diarylethylenes (stilbene-like) into angularly fused PAH (phenanthrene-like). We discovered the photocyclization of α -arylolefins, made chemically efficient by amine-induced proton tautomerism in the primary photoproduct (Lapouyade *et al* 1977), and extended this base-mediated 1,3-H-shift to the photocyclization of 1,2-diarylethylenes, leading to dihydro PAH (Lapouyade *et al* 1982b). We also investigated the cyclization of the 2-vinylbiphenyls (VB) from the singlet and the triplet excited states and from the radical cations (Lapouyade *et al* 1975, 1985, 1987; Fournier de Violet *et al* 1982).

In order to enlarge the field of PAH accessible by photocyclization of arylolefins, we present the main results of a systematic study on the mechanism of cyclization of these three structural types of arylolefins from the singlet and the triplet excited states and from the radical cations.

2. Photocyclization of α -arylolefins

2.1 1,1-Diarylethylenes

1-(α -Styryl)naphthalene (I) yields 1-phenyl acenaphthylene (II) by irradiation in the presence of iodine and oxygen (Lapouyade *et al* 1975). This cyclization is not triplet sensitized (nor quenched by oxygen) and is therefore ascribed to the singlet excited state. When amines are added to a degassed cyclohexane solution of I, the reaction is accelerated and 1-phenylacenaphthene (III) is the almost exclusive product. The catalytic capacity of the amines appears to correlate with their basicity and not with their ionization potential. The labelling experiments, as the fact that all the compounds which do not cyclize in the absence of amine, do not cyclize when it is present, argue in favour of a reversible cyclization which, in the absence of amine, very inefficiently gives II and III while amine generates an ion-pair which collapses into III (Lapouyade *et al* 1977) (scheme 1). Of the several 1-(α -styryl) arenes irradiated, only the naphthyl and the pyrenyl derivatives cyclized while, for example, the fluoranthenyl and the chrysenyl derivatives were photostable. This contrasting behaviour can be correlated with the fluorescence characteristics (figure 1): while the emission of the unreactive

Figure 1. Fluorescence and singlet excited state lifetime of 1-(α -aryl)olefins.

Table 1. Quantum yield^a of photocyclization of 1-(α -styryl)naphthalenes.

Σ'	Σ
	H	CN	OMe	NMe ₂	
	I	II	III V	IV VI	
H					
CN					

Compounds						
Solvent	I	II	III	IV	V	VI
C ₆ H ₁₂	0.31	0.12	10 ⁻²	< 10 ⁻³	< 10 ⁻³	< 10 ⁻³
CH ₃ CN	0.40	0.16	1.5 × 10 ⁻²	„	„	„

^aIrradiation at 373 nm of a 5×10^{-3} M solution of 1–VI with 0.22 M of 1,3-diaminopropane

compounds, illustrated by the α -styryl fluoranthene is similar to that of the parent arene (fluoranthene), the reactive compounds have a fluorescence spectra which has lost the vibrational structure of the parent arene, as illustrated by I, and their lifetime is very much shortened as expected for a singlet excited state with an additional non-radiative deactivation path. In other words, the unreactive compounds can be classified as the parent arenes with a substituent perturbation and the reactive ones as new chromophores including all the π electrons.

The simplest reactive system (I) has been substituted to reveal the electronic requirement for the reaction: the unsubstituted compound (I) cyclizes more efficiently and the derivatives which have a large charge transfer character in the excited state ($\mu_{IV}^* = 16.5_D$, Eckert *et al* 1988) do not photocyclize (table 1).

2.2 1-(α -Aryl)cycloalkenes

While the scope of the photocyclization of α -arylelefins with an acyclic double bond was rather narrow, two results led us to explore the photoreactivity of α -aryl cycloalkenes: in a preceding work we showed that when the triplet energy of the aryl group is high enough a perpendicular triplet state is formed and a *trans* double bond in the ground state ensues (Lazare *et al* 1984), and some years earlier (Dauben *et al* 1979), the high dienophile reactivity of a *trans* cyclohexene had been evidenced by an intramolecular Diels-Alder addition to 1-phenylcyclohexene.

With the cyclohexenyl derivatives, only the triplet energy of benzene is high enough to induce the formation of a perpendicular triplet (Lazare *et al* 1984) but naphthalene leads to the isomerization of the double bond of a cycloheptene or a cyclooctene cycle and cyclization follows (figure 2).

In the series 1-(α -aryl) olefins we have discovered two new types of photocyclization with very different structural restrictions: while fluoranthene and phenanthrene derivatives are not reactive in the singlet excited state, they cyclize by sensitization of the cycloheptenyl derivatives from the *trans* double bond (Lapouyade and Nourmamode 1984).

Figure 2. Reactivity and potential energy curves of 1-(α -aryl)cycloalkenes.

Figure 3. Stereochemistry of photocyclization of 1-(α -aryl)ethylenes.

The stereochemistry of these amine-mediated cyclizations⁸ is the result of the protonation of the benzylic anion from the less hindered side i.e. that of the vicinal hydrogen and consequently leads predominantly to the *cis* isomer particularly with the more hindered amines (figure 3).

3. Photocyclization of 1,2-diarylethylenes in primary amines

The amine-mediated 1,3-H-shift discovered with the photocyclization of 1-(α -styryl)naphthalene has been extended to the photochemical syntheses of dihydro PAH from

Figure 4. Comparative products of the photocyclization of orthomethylstilbenes under (a) oxidative conditions ($\text{O}_2 + \text{I}_2$), (b) non-oxidative conditions (RNH_2) followed by DDQ oxidation.

1,2-diarylethylenes (Lapouyade *et al* 1982b). From stilbene the predominant product is 1,4-dihydrophenanthrene (Couture *et al* 1975) while larger diarylethylenes give only compounds analogous to 9,10-dihydrophenanthrene. The mechanism of amine-promoted prototropy, in the intermediate dihydrophenanthrenes has been elucidated (Woning *et al* 1990). Beyond the access to dihydro PAH, amine prototropy reduces the loss of orthoalkyl groups during the photocyclization of orthoalkyl stilbenes (figure 4).

Unfortunately the regioselectivity of cyclization of metaalkyl stilbenes is not markedly changed by substituting iodine by amine and 2-alkyl and 4-alkyl phenanthrenes are formed unselectively.

If we consider 1-(α -naphthyl)1,2-diphenylethylene, the photocyclization could take place from the rotamers of two isomers (*E* and *Z*) to lead to three products. Whatever the trapping agent of the primary product of the photocyclization (iodine or amine) the relative yields of the three photoproducts are very close (figure 5), which is certainly due to a complete trapping of the photocyclized intermediates.

Figure 5. Photocyclization of 1-(α -naphthyl)1,2-diphenylethylene.

Figure 6. Photochemical synthesis of pentahelicene.

4. Cyclization of 2-vinylbiphenyls

While 4-methylphenanthrene is not regioselectively formed from the photocyclization of meta methylstilbene, irradiation of 2-vinyl-2'-methyl biphenyl leads to 4-methylphenanthrene only, certainly because the bay-interaction between the vinyl and methyl groups inhibits the formation of the corresponding rotamer.

We have earlier shown that a conrotatory cyclization followed by a 1,5-hydrogen shift accounts for the complete stereoselectivity of the singlet cyclization of 2-vinylbiphenyls (Lapouyade *et al* 1980). The sensitized reaction is often more efficient but is not stereoselective unless the double bond is part of a cyclopentene or a cyclohexene ring. When a 90° twist of the vinylic double bond is allowed, the resulting perpendicular triplet gives a non-stereospecific cyclization (Lapouyade *et al* 1985). A laser-flash photolysis study shows that the triplet cyclization is an adiabatic reaction giving a polyene in the triplet state (Lazare *et al* 1985; Bonneau 1986).

From the synthetic point of view the photocyclization of 2-vinylbiphenyls provides the route to a large number of monofluoroPAH (Lapouyade *et al* 1982a) and improves access to pentahelicene where the classical oxidative photocyclization of 1,2-di(β -naphthyl) ethylene inevitably leads to a mixture of pentahelicene and benzo-perylene (figure 6).

5. Reactivity of the arylethylene radical cations

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 (Belleville *et al* 1981). Owing to the bichromophoric character of several of the arylethylenes, one could expect that the radical cation of one part of the molecule could add electrophilically to the unsaturated, electron-rich other part. As ground-state oxidizers, we have used *tris*-(4-bromophenyl) aminium hexachloroantimonate, and as photochemical oxidizers, cyano-arenes in the singlet excited state and quinones in the triplet excited state.

5.1 1,2-Diarylethylene radical cations

Whatever the oxidant, 1,2-diarylethylenes lead only to *cis* $\rightleftharpoons$ *trans* isomerization, and when only the *cis* isomer exists, as in 1,2-diphenylcyclopentene, the starting compound is recovered.

Figure 7. Reactivity of 1-(α -styryl)naphthalene radical cation.

Figure 8. Reactivity of 2-vinylbiphenyl radical cations.

5.2 1,1-Diarylethylene radical cations

1,1-diarylethylenes with a vacant *peri* position, where a cyclization could be expected to occur, do not lead to any intramolecular reaction, but instead to [2 + 2] and [2 + 4] cycloadditions, as has been observed with 1,1-diphenylethylene (Mattes and Farid 1986).

We have observed this chemistry, illustrated with I (figure 7), with several 1-(α -styryl) arenes. When the oxidant is an excited cyanoarene, we also separate a dehydrogenated [4 + 2] cycloaddition product and the reduced sensitizer.

5.3 2-Vinylbiphenyl radical cations

With 10% of *tris*-(4-bromophenyl)aminium hexachloroantimonate in methylene chloride, 2-vinylbiphenyls lead to 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, stoichiometrically gives phenanthrene derivatives. With photochemical oxidants, only phenanthrenes or 9,10-dihydrophenanthrenes are obtained (Lapouyade *et al* 1987) (figure 8).

6. Conclusion

We have discovered the photocyclization of α -aryl olefins mediated by primary amines and delineated its scope according to whether the double bond is acyclic or is part of a cycloalkene. In the 1,2-diarylethylene series, irradiation in presence of amine leads to dihydro PAH and protects the alkyl group in the ortho-position against

elimination after cyclization. With 2-vinylbiphenyl compounds the stereochemistry of the cyclization is a function of the excited state multiplicity and from the radical cation, electrocyclization can be pursued by a protic catalysis.

Three structural types of arylelefins have been evaluated as precursors for the photochemical formation of PAH.

References

- Belleville D S, Wirth D W and Bauld N L 1981 *J. Am. Chem. Soc.* **103** 718
Bonneau R 1986 *New J. Chem.* **10** 425
Couture A, Lablache-Combier A and Ofenberg H 1975 *Tetrahedron* **31** 2023
Dauben W G, Van Riel H C H A, Hauw C, Leroy F, Jousset-Dubien J and Bonneau R 1979 *J. Am. Chem. Soc.* **101** 1901
Eckert C, Heisel F, Miehe J A, Lapouyade R and Ducasse L 1988 *Chem. Phys. Lett.* 357
Fornier de Violet P, Lapouyade R and Rayez J C 1982 *J. Photochem.* **19** 253
Laarhoven W H 1983 *Rec. Trav. Chim., Pays-Bas* **102** 185
Lapouyade R, Hanafi N and Morand J -P 1982a *Angew. Chem., Int. Ed. Engl.* **21** 766
Lapouyade R, Koussini R and Bouas-Laurent H 1977 *J. Am. Chem. Soc.* **99** 7374
Lapouyade R, Koussini R, Nourmamode A and Courseille C 1980 *J. Chem. Soc., Chem. Commun.* 740
Lapouyade R, Koussini R and Rayez J-C 1975 *J. Chem. Soc., Chem. Commun.* 676
Lapouyade R, Manigand C and Nourmamode A 1985 *Can. J. Chem.* **63** 2192
Lapouyade R and Nourmamode A 1984 *Synthesis* 161
Lapouyade R, Veyres A, Hanafi N, Couture A and Lablache-Combier A 1982b *J. Org. Chem.* **47** 1361
Lapouyade R, Villenave P, Nourmamode A and Morand J -P 1987 *J. Chem. Soc., Chem. Commun.* 776
Lazare S, Bonneau R and Lapouyade R 1984 *J. Phys. Chem.* **88** 18
Lazare S, Lapouyade R and Bonneau R 1985 *J. Am. Chem. Soc.* **107** 6604
Liu L, Yang B, Katz T J and Poindexter K 1991 *J. Org. Chem.* **56** 3769
Mallory F B and Mallory C W 1984 *Org. Synth.* **30** 1
Mattes S L and Farid S 1986 *J. Am. Chem. Soc.* **108** 7356
Woning J, Weisenborn P C M, Varma C A G O and Laarhoven W H 1990 *J. Photochem. Photobiol* **A55** 169