Intramolecular aryl rearrangement in the photolysis of alken-1-yl aryl methyl phosphates

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Upon UV-irradiation of alken-1-yl aryl methyl phosphates in methanol a cationic migration of an aryl group to a neighbouring olefinic moiety to produce arylalkanone and arylalken-1-yl methyl ether has been observed.

Several types of photochemical reaction of aryl phosphates are known. Firstly, photochemical nucleophilic substitution induced by the attack of a nucleophile such as Cl^- has been observed in an aryl phosphate.[1] Secondly, upon photoirradiation of the di- or tri-aryl phosphate, in which two or three aryl groups exist in close proximity to each other, coupling and rearrangement between the two aryl groups has occurred through an intramolecular excited complex to produce a biaryl derivative.[2] Thirdly, an intramolecular photochemical reaction of allyl diphenyl phosphate has been shown to produce 2-allylphenyl phenyl phosphate[3] through an abstraction of the allylic hydrogen.[4]

Here we report a novel type photoreaction of alken-1-yl aryl methyl phosphates **1** in which α-arylalkanone **2** and arylalken-1-yl methyl ether **3** were produced *via* a cationic aryl migration.

Upon UV-irradiation of (*E*)-1-methylpropen-1-yl 4-methoxyphenyl methyl phosphate **1a** in methanol, 3-(4-methoxyphenyl)butan-2-one **2a**, (*E*)-2-(4-methoxyphenyl)-1-methylpropen-1-yl methyl ether **3a** and (*Z*)-1-methylpropen-1-yl 4-methoxyphenyl methyl phosphates **1a′** were obtained.[†] The formation of the trimethyl phosphate **4** was also observed by a GC-MS analysis after methylation of the photolyzed mixture using diazomethane.

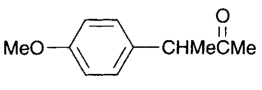
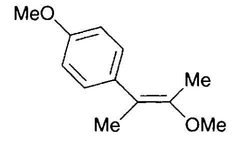
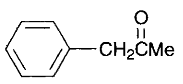
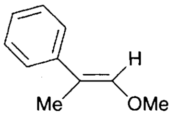
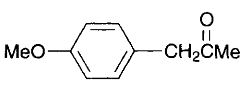
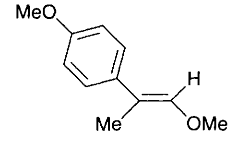
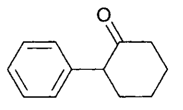
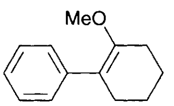
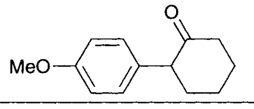
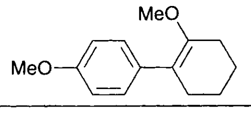
A similar photochemical reaction was observed on other alken-1-yl aryl methyl phosphates **1b–e** in methanol, and α-arylalkanones **2b–e** and 2-arylalken-1-yl methyl ethers **3b–e** were formed.[†] The results are shown in Tables 1 and 2. The characteristics of the photoreaction of **1** are summarized as follows: (i) the presence of an electron donating *p*-methoxyl substituent enhances the reactivity of **1**, (ii) the product

Table 2 Photolysis of **1a** and **1c** in various solvents[a]

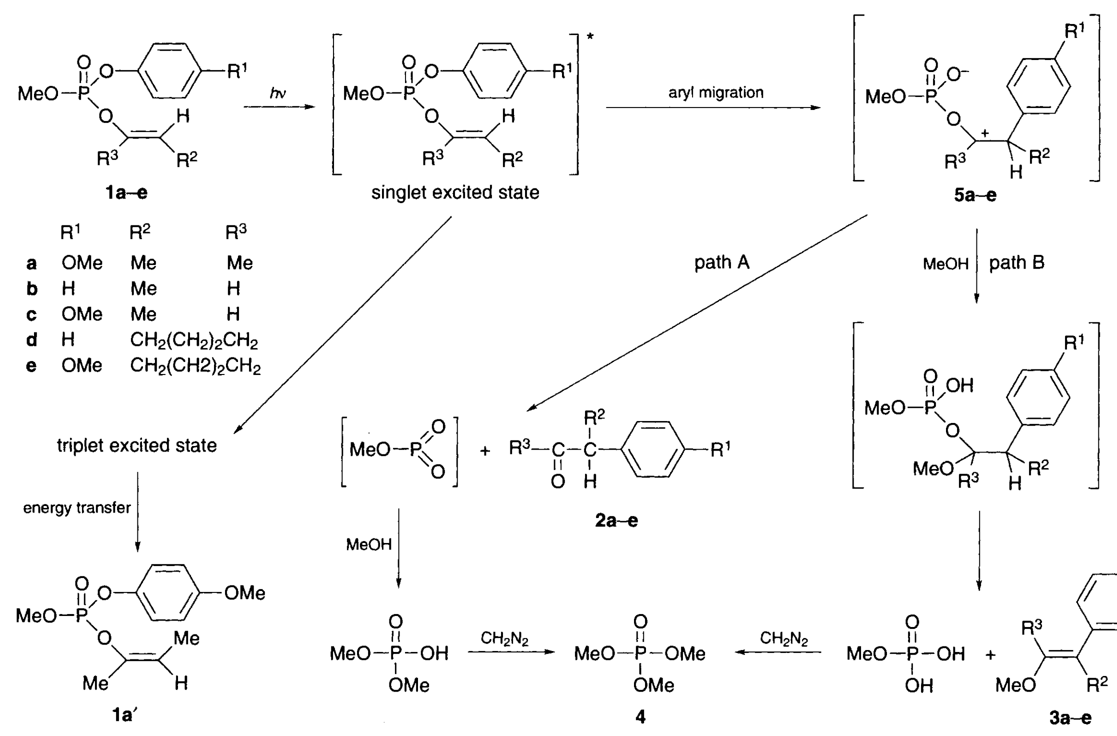
	1a				**1c**	
		Yield (%)				
Solvent	Conversion (%)	**2a**	**3a**	**1a′**	Conversion (%)	Yield of **2c** (%)
MeOH	80	25	16	14	80	56
EtOH	70	13	—	18	75	20
THF	67	6	—	29	40	6
C_6H_{12}	51	2	—	33	38	4

[a] Irradiated in deaerated solution (1.0 × 10^{-2} mol dm^{-3}) for 30 min.

Table 1 Conversions, product yields and product quantum yields (ϕ)[a] on photolysis of **1** in methanol

Substrate	Conversion (%)	**2**	Yield (%)	($\phi_2 \times 10^2$)	**3**	Yield (%)	($\phi_3 \times 10^2$
1a	83		25	(1.0 ± 0.2)		16	(0.7 ± 0.1)
1b	52		31	(2.0 ± 0.3)		trace	—
1c	80		56	(2.4 ± 0.2)		trace	—
1d	70		18	(1.0 ± 0.1)		28	(1.2 ± 0.2)
1e	85		20	(1.3 ± 0.2)		32	(1.5 ± 0.3)

[a] The quantum yields determined at several concentrations of **1** (3.0 × 10^{-3}–2.0 × 10^{-2} mol dm^{-2}).



	R^1	R^2	R^3
a	OMe	Me	Me
b	H	Me	H
c	OMe	Me	H
d	H	$CH_2(CH_2)_2CH_2$	
e	OMe	CH2(CH2)2CH2	

Scheme 1

distribution depends on the structure of the substrate (the product ratio of **3**:**2** increased in the order **1b** ≈ **1c** < **1a** < **1d** ≈ **1e**), (iii) the formation of **2** and **3** proceeds in intramolecular processes [the quantum yields of **2** and **3** were unaffected by the concentration (3.0×10^{-3}–2.0×10^{-2} mol dm^{-3}) of **1**[‡]], and (iv) the photoreaction proceeds through an ionic intermediate (in non-polar cyclohexane, the photoreactivity of **1** was considerably reduced).

In order to clarify the photochemical reaction, fluorescence quenching experiments were carried out. The fluorescence spectrum of **1a** (λ_{max} 310 nm) showed no interaction between the aryl and alkenyl groups at the excited state, and the fluorescence was quenched by oxygen in methanol. A Stern–Volmer analysis provided a good linear correlation between I_f^0/I_f (I_f = fluorescence intensity) and $[O_2]$, from which $k_q\tau = 121$ mol^{-1} dm^3 (correlation coefficient $r = 0.995$) was obtained. The formation of products was quenched by oxygen with similar $k_q\tau$ values of 124 ($r = 0.990$) and 125 ($r = 0.992$) mol^{-1} dm^3 for **2a** and **3a**, respectively. Therefore, the formation of **2a** and **3a** takes place *via* the singlet excited state of **1a**.[¶]

On the basis of these observations, the following mechanism is proposed for the photolysis of **1** (Scheme 1). The cationic migration of the aryl group to a neighbouring olefinic moiety produces an intermediate **5** through the singlet excited state of **1**. The product **2** is produced by P–O bond cleavage (β-bond to the cationic centre) (path A). On the other hand, the product **3** is produced by the nucleophilic attack of methanol to **5**, followed by the elimination of methyl dihydrogen phosphate (path B). In these competitive reaction paths, the product ratio, **3**:**2**, was dependent on the structure of **1**; the ratio increased in the order **1b** ≈ **1c** < **1a** < **1d** ≈ **1e**. This order inversely correlates with the number of β-H to the cationic centre in **5** which contributes to the delocalization of the positive charge due to inductive and conjugative effects. This stabilization of the cationic centre of **5**, expected especially in **5b** and **5c**, may reduce the bimolecular nucleophilic reaction by methanol and the unimolecular path A is favoured. Enhancement of the reactivity induced by solvent polarity and an electron donating *p*-methoxy substituent supports the aryl cationic migration.

We have demonstrated a novel aryl-1,5-photorearrangement of alken-1-yl aryl methyl phosphate and revealed the reaction mechanism through the cationic migration of an aryl group. The present reaction may be useful for the formation of a carbon-aryl bonds in organic synthesis.

Footnotes

[†] Photolysis was carried out in a quartz cell and irradiated using a 300 W medium-pressure mercury lamp at 20–25 °C for 30 min. The reaction mixture was analyzed by GLC and GC-MS directly or after methylation with diazomethane.

[‡] Quantum yields were measured using a 60 W low-pressure mercury lamp, and actinometry was performed using potassium trioxatoferrate(III) solution.[5]

[¶] As for the formation of **1a′**, *via cis-trans* isomerization, intramolecular triplet energy transfer[6] may take place, because the Stern–Volmer plot for **1a′** did not provide a linear correlation.

References

1 E. Havinga and R. O. de Jongh, *Bull. Soc. Chim. Belg.*, 1962, **71**, 803; E. Havinga, R. O. de Jongh and M. E. Kronenberg, *Helv. Chim. Acta*, 1967, **50**, 2550; R. O. de Jongh and E. Havinga, *Recl. Trav. Chim. Pag-Bas.*, 1968, **87**, 1318, 1327; M. Nakamura, Y. Osako, Y. Okamoto and S. Takamuku, *Phosphorus Sulfur Silicon Relat. Elem.*, 1993, **85**, 141.

2 R. A. Finnegann and J. A. Matson, *J. Am. Chem. Soc.*, 1972, **94**, 4780; M. Shi, K. Yamamoto, Y. Okamoto and S. Takamuku, *Phosphorus Sulfur Silicon Relat. Elem.*, 1991, **60**, 1; Y. Okamoto, M. Nakamura, M. Shi and S. Takamuku, *Photochem. Photobiol.*, 1992, **56**, 403; M. Nakamura, K. Sawasaki, Y. Okamoto and S. Takamuku, *J. Chem. Soc., Perkin Trans. 1*, 1994, 141; M. Nakamura, M. Shi, Y. Okamoto and S. Takamuku, *J. Photochem. Photobiol. A*, 1995, **85**, 111.

3 D. R. Anderson and C. N. Eley, *Tetrahedron Lett.*, 1989, **30**, 4059.

4 W. G. Bentrude, S.-G. Lee, K. Akutagawa, W. Ye and Y. Charbonnel, *J. Am. Chem. Soc.*, 1987, **109**, 1577; N. Suzuki, T. Kawai, S. Inoue, N. Sano and Y. Izawa, *Bull. Chem. Soc. Jpn.*, 1980, **53**, 1421; C. E. Giffin, W. G. Bentrude and G. M. Jhonson, *Tetrahedron Lett.*, 1969, 969; P. J. Wagner, *Acc. Chem. Res.*, 1971, **4**, 168.

5 C. G. Hatchard and C. A. Parker, *Proc. R. Soc. London*, 1956, **A235**, 518.

6 C. S. Nakagawa and P. Sigal, *J. Chem. Phys.*, 1970, **52**, 3277; C. S. Nakagawa and P. Sigal, *J. Chem. Phys.*, 1970, **53**, 2993; D. O. Cowan and A. A. Baum, *J. Am. Chem. Soc.*, 1970, **92**, 2154; W. Ferree, Jr., J. B. Grutzner and H. Morrison, *J. Am. Chem. Soc.*, 1971, **93**, 5502.

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