

Photolysis of Bis(methoxyphenyl) Methylphosphonates. Their Emission Spectra and Formation of Dimethoxybiphenyl and Dimethoxy-9,10-dioxaanthracene.

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Key words: *Bis(methoxyphenyl) methylphosphonate; dimethoxybiphenyl; dimethoxy-9,10-dioxaanthracene; intramolecular excimer; fluorescence*

Summary: *Upon UV-irradiation in methanol, bis(methoxyphenyl) methylphosphonates underwent an intramolecular coupling of two methoxyphenyl groups to give dimethoxybiphenyls and dimethoxy-9,10-dioxaanthracenes. The reactivities and fluorescence spectra of the phosphonates were sensitive to the position of the methoxy group. These photo-induced couplings proceed probably through the formation of the two types of singlet intramolecular excimers.*

It has been reported that upon UV-irradiation in methanol, tris(4-methoxyphenyl) phosphate (1) underwent an intramolecular coupling of two 4-methoxyphenyl groups to give 4,4'-dimethoxybiphenyl (2a) and 4-methoxyphenyl phosphate.¹⁾ However, the reaction mechanism has been still ambiguous. We also reported that upon irradiation of bis(4-methoxyphenyl) triphenylmethylphosphonates, three kinds of biaryls, homocoupled biphenyl and 2a and cross-coupled 4-methoxybiphenyl, were given.²⁾ These interesting findings stimulate us further to study the reaction mechanism. Herein we wish to report the photolysis and the fluorescence behaviors of three positional isomers of bis(methoxyphenyl) methylphosphonates (3a-c).³⁾ The formation mechanism of 9,10-dioxaanthracene derivatives will be also speculated.

After irradiation of 3a-c in methanol with a high pressure mercury lamp under argon atmosphere for 1 h, the products were analyzed by GLC (2% Silicone OV-17 on Chrom WAW DMCS 60/80 mesh, Shimadzu 7A) directly or after treatment with an ethereal solution of diazomethane and confirmed in agreement with authentic samples prepared by other methods.⁴⁾ It was noted that the phosphonate 3a-c gave not only expected dimethoxybiphenyls (2a-c) and dimethyl methylphosphonate (4), but dimethoxy-9,10-dioxaanthracenes (5a-c) and methyl methylphosphinate (6), which was probably derived from an intermediate, methylphosphinidene oxide (7),⁵⁾ by trapping with methanol (Scheme 1). The phosphonate 3a gave 2a as a major product (70%) and 5a as a minor product (4%), while 3c gave 2c and 5b in approximately

equal amount yields (20 and 16%, respectively). The yield of **2** decreased and that of **5** increased in the sequence, $3a > 3b > 3c$. The phosphonate **3b** gave two isomers, **5a** and **5c**, which were the regio-isomers of methoxy groups. Their chemical and quantum yields are summarized in Table 1.

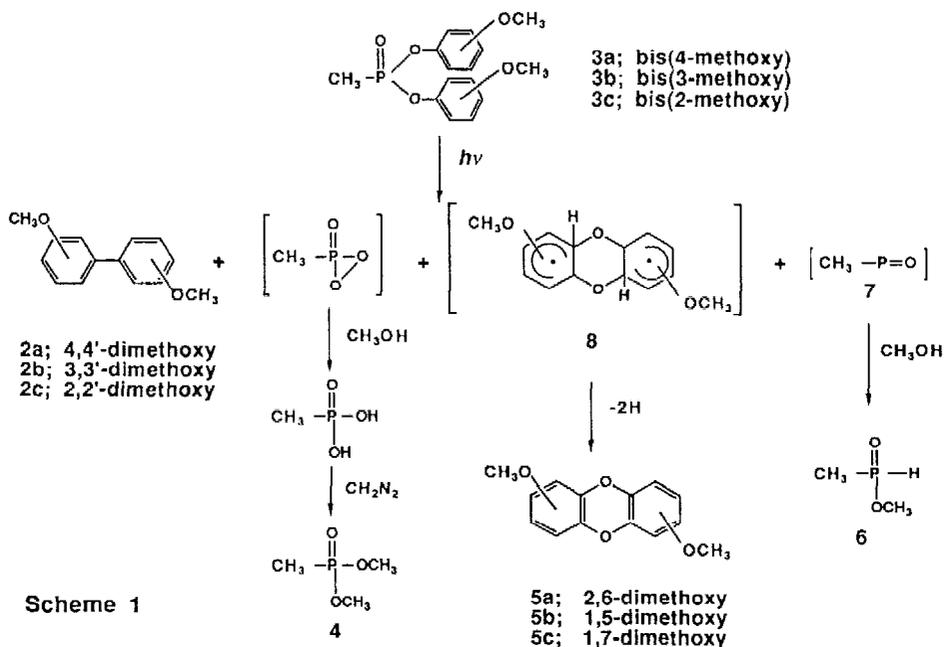


Table 1. Photolysis of **3a-c**.^{a)}

Compd.	Conv./%	ϕ ^{b)}	Products (Yield/%)			
3a	73	0.12	2a (70)	4 (64)	5a (4)	6 (trace)
3b	50	0.06	2b (37)	4 (30)	5a (9), 5c (3)	6 (5)
3c	40	0.04	2c (20)	4 (16)	5b (16)	6 (12)

a) Irradiated in methanol (1.0×10^{-2} mol dm⁻³) in a quartz tube for 1 h under argon atmosphere by use of a 300 W high pressure Hg lamp. b) The quantum yield of **2** at 254 nm. The photolyses were settled within 5% conversion.

Emission spectra of **3a-c** are shown in Figure 1. It is clear that the substitution position of methoxy group on benzene ring so markedly affected their emission spectra. Although the absorption spectra of **3a-c** were similar to those of the corresponding diethyl methoxyphenyl phosphates, the emission spectra of **3a** or **3b** consisted of two bands at 320 and 380 nm or 300 and 345 nm, respectively. The relative intensities of two bands of **3a** or **3b** were independent on its concentration. They had the similar characteristics to those of monomer and intramolecular excimer

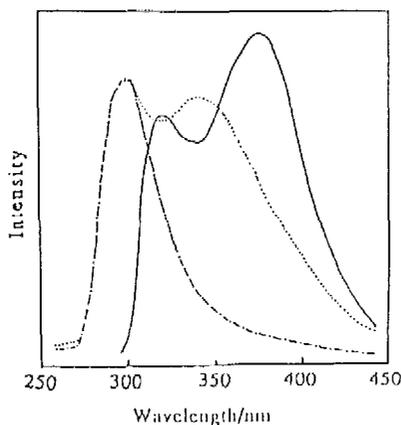


Figure 1. Emission spectra of 3a-c in methanol (10^{-4} mol dm $^{-3}$), λ_{ex} =280 nm.
3a; ——— 3b; 3c; - - -

of two aromatic rings in compounds of the type A-(CH $_2$) $_n$ -A, in which often for $n=3$ an optimal situation is obtained.^{6, 7)}

Therefore, the long-wavelength emission band must be due to an intramolecular excimer between two methoxyphenyl groups. These results indicate that Hirayama's rule can be also applied to the molecule having two chromophores separated by three heteroatom chains (-O-P-O-).

The fluorescence of 3a and the formation of 2a in methanol were quenched efficiently by molecular oxygen. From Stern-Volmer analysis,⁸⁾ $k_{qE}\tau_E=222$ and $k_{qM}\tau_M=51$ dm 3 mol $^{-1}$ for quenching excimer and monomer emission were obtained, respectively, where k_{qE} and k_{qM} are oxygen quenching rate constants for the excimer and the monomer, and τ_E and τ_M are the life-times of the eximer and the monomer, respectively. On the other hand, $k_{q1}\tau_1=262$ dm 3 mol $^{-1}$ for quenching the formation of 2a was obtained, where k_{q1} and τ_1 are an oxygen quenching rate constant and a life-time for the active species giving 2a, respectively. The value $k_{qE}\tau_E$ was approximately equal to the value $k_{q1}\tau_1$. The formations of 2b-c from 3b-c were also quenched with oxygen, respectively. Therefore, this result indicates that the photo-induced biaryl coupling probably proceeds via a singlet intramolecular excimer state. But the yield of 5a from 3a was hardly affected with oxygen. In an emission spectrum of the ortho methoxy derivative 3c, an excimer emission band was hardly observed and the total emission spectrum resulted mainly in that of the monomer. The yield of 5b from 3c was not also affected by oxygen. The excited species giving 5 may be different from that giving 2. The life-time of the former species may be shorter than that of the latter species. The difference between the dipole moments of a *o*-methoxyphenoxy group and a *p*-methoxyphenoxy group must cause a great

difference on the situation of the interaction between these aryl groups. In the excited state, the interaction between the aryl groups may occur in the manner counteracting any increase in dipole moment.⁸⁾ In the case of **3a**, which the aryl group has not an effective dipole moment, the intramolecular interaction may occur in the manner of face to face or π - π interaction, while in the case of **3c**, which the aryl group has a significant dipole moments, the interaction may be occur in the manner of n - π interaction,⁹⁾ that is, the interaction between the lone pair electron of oxygen of Ar-O-P and π -electron of the aromatic ring will be enhanced to facilitate the bonding of Ar-O-Ar and to result in the formation of a biradical intermediate (**8**), which in turn is easily oxidized to **5** (Scheme 1).

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References and Notes

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- (3) The compounds **3a-c** were prepared by the reaction of methylphosphonyldichloride with the corresponding methoxyphenols, respectively, in the same procedure as reported previously, [E. Cherbuliez, "Organic Derivatives of Phosphoric and Polyphosphoric Acid" in "Organic Phosphorus Compounds," Vol. 6, ed. by G. M. Kosolapoff and L. Maier, Wiley-Interscience, New York, 1973, p. 220]. The products were purified by chromatography on silica gel column (eluent; chloroform:hexane=1:3). **3a-c** as colorless oil. **3a**: $UV_{\max}(\text{MeOH})$ 278 nm (ϵ 4680 $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$); **3b**: $UV_{\max}(\text{MeOH})$ 271 nm (ϵ 4800 $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$); **3c**: $UV_{\max}(\text{MeOH})$ 271 nm (ϵ 5180 $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$).
- (4) Products **5a, b**, and **c** and **6** were prepared by the known procedures; M. Tomita and J. Yagi, *J. Pharm. Soc. Jpn.*, **78**, 581 (1958); K. Sasse, "Organische Phosphorverbindungen Teil I" in "Methoden der Organischen Chemie" ed. E. Muller, Georg Thieme, Stuttgart (1963) p. 323. The others were commercially available.
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- (6) Although the absorption spectrum of **3a** [$UV_{\max}(\text{MeOH})$ 278 nm] was similar to that of methyl 4-methoxyphenyl methylphosphonate (**9**), their emission spectra were in different aspect each other. In the case of **9**, only one emissions band was observed at 310 nm, but **3a** exhibited two emission bands at 320 and 380 nm as described above. The phosphonate **9** was quite stable upon prolong UV-irradiation under the same conditions. The emission spectrum of phosphate **1** in methanol was also similar to that of **3a**, although its relative intensity of the excimer emission to the monomer emission was much more large.
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