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The Photo-Arbuzov Rearrangement of Dimethyl 9-Anthrylmethyl Phosphite and the Photodimerization of the Corresponding Phosphonate

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ABSTRACT

*Upon irradiation, 9-anthrylmethyl phosphite (***2***) undergoes the photo-Arbuzov rearrangement to give the corresponding phosphonate* **3**. *Prolonged irradiation led to the clean formation of the centrosymmetric, head to tail, [4 + 4] photocycloaddition product* **4** *as indicated by X-ray crystallographic analysis. The same photodimer results on irradiation of phosphonate* **3** *itself in solution or in the solid phase. Phosphite* **2** *does not undergo photodimerization to* **6**. © 1998 John Wiley & Sons, Inc. Heteroatom Chem 9:155–160, 1998

INTRODUCTION

It has been discovered in our research group that benzyl phosphites readily undergo photochemical Arbuzov rearrangement to benzylphosphonates upon irradiation with UV light [1,2]. The application of this rearrangement to the synthesis of acyclic nucleoside-based phosphonates has been demonstrated [3,4]. A study of the stereochemistry of the photorearrangement of **1** showed it to proceed with near exclusive retention of configuration at the chiral carbon when X = OR [1,5,6]. When X = NR_2, however, a higher degree of stereorandomization was observed. The naphthyl phosphite analogs of **1** have been shown to efficiently undergo the photo-Arbuzov rearrangement as well [5,6]. Recently, the dynamics of the interactions of triplet radical pairs, generated from the triplet excited states of benzyl and 1-naphthylmethyl phosphites, have been investigated by CIDEP [7] and ^{31}P CIDNP [8] techniques.

We now report the efficient photorearrangement of 9-anthrylmethyl dimethyl phosphite (**2**) to yield the corresponding phosphonate (**3**) that upon further irradiation yields head-to-tail 9,10-anthracene photodimer **4.** The photodimerization of anthracene has been extensively studied since its discovery by Fritzsche in 1866 [9–12]. Detailed studies on the mechanism of dimerization are summarized in several reviews [13,14].

Indeed, 9-substituted anthracenes are generally found to undergo head-to-tail photodimerization in solution involving the central ring of the anthracene π system to give photodimer **5.** Photodimerizations of anthracene and its derivatives have also been found to occur in the solid state [15–22]. The stereochemistry, head-to-tail vs. head-to-head, of the formation of photodimers in the solid phase has been shown to be influenced by the contact geometries of nearest-neighbor molecules in the unit cell [13–15].

Dedicated to Prof. William E. McEwen on the occasion of his seventy-fifth birthday.

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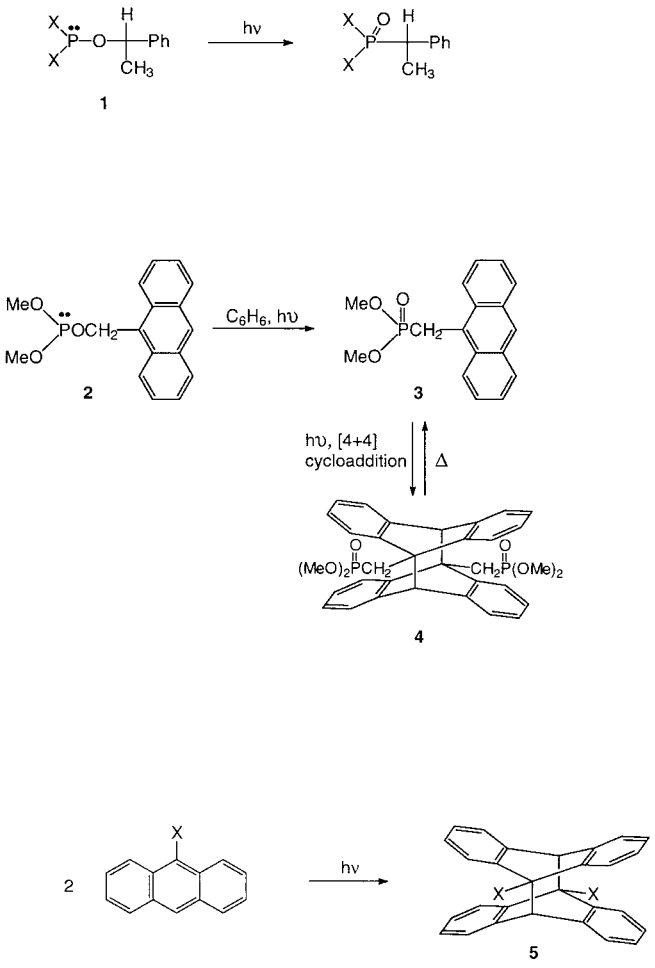


SCHEME 1

RESULTS AND DISCUSSION

The irradiation (Pyrex) of a 0.3 M solution of **2** (δ ^{31}P = 140.1) in deoxygenated benzene, using a 450 W medium-pressure Hanovia lamp equipped with a uranium filter, proceeded cleanly to give phosphonate **3** (δ 28.2) as evidenced by ^{31}P NMR spectroscopy. Upon further irradiation, after most of the starting phosphite **2** had been consumed, a somewhat broadened ^{31}P NMR signal (δ 30.3) was observed in the phosphonate region. Prolonged irradiation resulted in increasing amounts of this material (**4**) and >90% disappearance of phosphonate **3.** The signal at δ 30.3 was also obtained when phosphonate **3,** separated from the photolytic mixture of **2,** was independently irradiated with the same light source (0.01 M in benzene). No other peaks were seen in the ^{31}P NMR spectrum during any stage of irradiation.

Isolation by HPLC of the secondary photolytic product from the irradiation of **3** gave a white solid (**4**) with the same elemental composition as phosphonate **3** but with twice its molecular weight (MS). X-ray quality crystals were obtained as colorless prisms, grown by diffusion of pentane into an ethereal solution of **4.** The X-ray crystal structure of **4,** the head-to-tail dimer of **3,** is shown in the ORTEP diagram of Figure 1. Upon GC injection, a solution of **3** and **4** gave only one peak, corresponding to monomer **3.** The same signal was seen on injection of a solution of pure phosphonate **4.** This shows the photodimerization to be a *thermally reversible* process (**4** $\rightarrow$ **3**) as also noted for other anthracene dimers [23].

Significantly, during irradiation of phosphite **2,** no new signal in the ^{31}P NMR region typical of phosphites was observed. This shows conclusively that phosphite **2** first undergoes the photo-Arbuzov reaction to give the corresponding phosphonate **3** that then dimerizes upon prolonged irradiation to yield **4.** Thus, the anthracene moiety of phosphite **2** *does not* first undergo photodimerization to give dianthracene phosphite **6,** followed by photo-Arbuzov rearrangement of **6** to yield **4.**

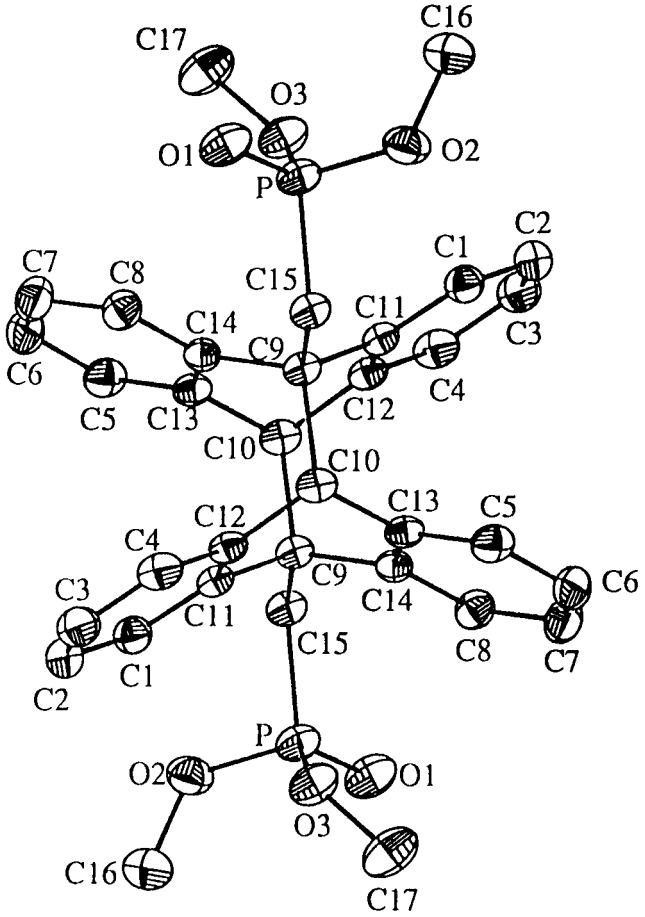
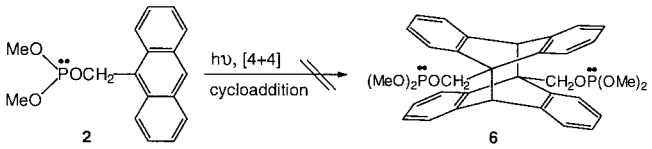


FIGURE 1 ORTEP drawing of the X-ray crystal structure of **4.**



SCHEME 2

Evidently, the photodimerization of **2** is slower than its photo-Arbuzov rearrangement to **4.** Additionally, dimer **6** no longer contains the arylmethyl phosphite structure required for the photo-Arbuzov processes characteristic of the benzyl and 1-naphthylmethyl analogs. Even if it were formed, dimer **6,** therefore, would not be expected to undergo photo-Arbuzov rearrangement.

The head-to-tail photodimer **4** was also obtained on the irradiation of recrystallized phosphonate **3** in the solid state. In solution, head-to-head photodimers generally are not formed due to steric hindrance [14]. However, molecular packing patterns can influence the stereochemistry of dimerization of 9-substituted anthracenes in the solid phase [15–22]. This pattern for phosphonate **3** (Figure 2) shows the molecules to be oriented in a manner that favors the experimentally observed head-to-tail dimer formation.

TABLE 1 Crystal Data for **4**

Mole formula	$P_2O_6C_{34}H_{34}$
Mole weight	600.595
Space group	$P2_1/c$ (no. 14)
Crystal system	monoclinic
Cell dimensions	
a, Å	9.527 (3)
b, Å	16.832 (6)
c, Å	9.640 (2)
b, deg	113.58 (2)
n, Å^3	1416.74
Z	2
D_{calcd}, g/cm^3	1.408
Absorption coefficient, cm^{-1}	1.943
Radiation, Å	1 (Mo) 0.71073
2q range, deg	4.00–50.00
Scan technique	q/2q
Scan width, deg	0.8000 + 0.3500 tan q
Data to parameter ratio	7.903
Shift to error ratio	0.004
R	0.0336
R_w	0.0477

TABLE 2 Crystal Data for **3**

Mole formula	$P_1O_3C_{17}H_{17}$
Mole weight	300.297
Space group	$P2_1/c$ (no. 14)
Crystal system	monoclinic
Cell dimensions	
a, Å	12.115 (4)
b, Å	12.114 (1)
c, Å	10.335 (3)
b, deg	100.41 (2)
n, Å^3	1491.87
Z	4
D_{calcd}, g/cm^3	1.337
Absorption coefficient, cm^{-1}	1.845
Radiation, Å	1 (Mo) 0.71073
2q range, deg	4.00–50.00
Scan technique	q/2q
Scan width, deg	0.8000 + 0.3400 tan q
Data to parameter ratio	7.066
Shift to error ratio	0.013
R	0.0479
R_w	0.0658

SUMMARY

9-Anthrylmethyl dimethyl phosphite (**2**) has been shown to readily undergo the photo-Arbuzov rearrangement. Significantly, the rate of photodimerization of **2** via [4 + 4] photocycloaddition of the anthracene moiety of **2** to form **6** is much slower than its rate of unimolecular photo-Arbuzov rearrangement to **3.** The stereochemistry of the [4 + 4] photocycloaddition dimerization of **3** is head-to-tail to yield centrosymmetric **4** both in solution and in the solid phase.

EXPERIMENTAL

General Procedures and Materials

Air-sensitive materials were transferred by syringe or cannula or in a glove bag under an argon atmosphere. Commercial solvents (spectrophotometric grade) were used as received unless otherwise noted, except for distillation prior to use. Diethyl ether was

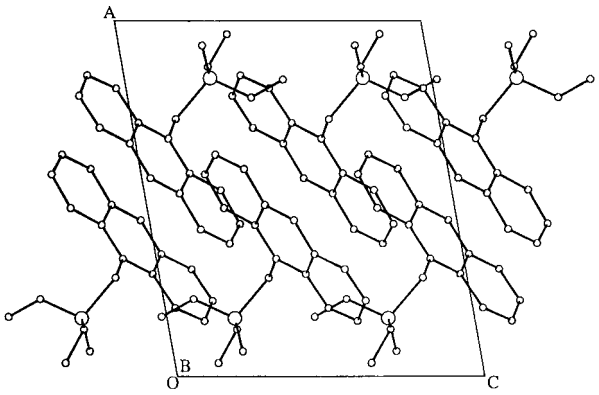


FIGURE 2 Packing diagram for **3.**

dried over sodium/benzophenone. Acetonitrile, methanol, and *n*-pentane were purchased as OmniSolv grade. Flash chromatography was conducted on Silica Gel 60, 230–400 mesh, obtained from EM Science with the solvent system indicated. Microanalyses were performed by Atlantic Microlab, Inc., Norcross, Georgia. High-performance liquid chromatographic (HPLC) separations of products were obtained under isocratic conditions with a Waters 590 solvent delivery system equipped with an ISCO V^4 UV Absorbance Detector, using a 4.6 mm ID analytical, a 10 mm ID semipreparative, or a 21.4 mm ID preparative Dynamax® HPLC column (100 A° spherical Microsorb packings in 5 mm particle size, Rainin Instrument Co., Inc.), equipped with guard columns.

Spectroscopic and Physical Data

Proton (^{1}H), carbon (^{13}C), and phosphorus (^{31}P) nuclear magnetic resonance (NMR) spectra were obtained in $CDCl_3$ or C_6D_6 on Varian Unity and XL-300 spectrometers. Chemical shifts (δ) are reported in parts per million relative to tetramethylsilane (0.00 ppm) with the solvent as an internal standard for ^{1}H and ^{13}C NMR. A capillary of phosphoric acid (H_3PO_4) in the appropriate solvent was used as an external reference (0.00) for the ^{31}P spectra. Multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Melting points were determined using a Thomas Hoover melting-point apparatus and are uncorrected. Ultraviolet (UV) spectra were obtained in acetonitrile solutions on a Hewlett-Packard 8452A Diode Array Spectrophotometer. Wavelength maxima (λ_{max}) are reported in nm. Extinction coefficients (ε) are reported in L mol^{-1}cm^{-1}. Low- and high-resolution mass spectrometries (LRMS and HRMS, EI, 70 eV) were performed on a Finnigan MAT 95 gas chromatograph/mass spectrometer operated in the EI and CI modes. GC/MS spectra were taken on a Hewlett-Packard 5890A GC, with a Hewlett Packard 5970 MSD, 15 m $\times$ 0.25 mm $\times$ 0.25 mm DB-1 capillary column.

X-ray Crystallography

A single crystal of **4** was mounted on a CAD4 diffractometer for data collection. Cell constants were obtained from 25 reflections within $25 < 2q < 30$. The space group was determined from systematic absence ($h0l$, $l = 2n$; $0k0$, $k = 2n$) and subsequent least-squares refinement to be $P2_1/c$. Standard reflections showed no decay during data collection. Lorentz and polarization corrections and an empirical absorption correction, based upon a series of ψ scans, were applied to the data. Intensities of equivalent reflections were averaged. The structure was solved by standard direct methods with the Molen/VAX package. Nonhydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were located and refined isotropically. Scattering factors [24] and D*f* ′ and D*f* ″ values [25] were taken from the literature [26].

Procedure for the Solution Photochemistry of Phosphite **2**

A solution of 9-anthrylmethyl dimethyl phosphite (**2**) in deoxygenated benzene (ca. 0.03 M) was prepared under an argon atmosphere. The solution in a Pyrex tube was irradiated through a uranium filter ($\lambda > 320$ nm) using a 450 W medium-pressure Hanovia lamp. The reaction was monitored by GC and ^{31}P NMR spectroscopy. More than 90% of the starting phosphite was consumed in 3 hours. In this reaction and the others subsequently described, no other peaks were noted in the ^{31}P NMR spectrum. Product phosphonate **3** was isolated by HPLC (1.5% methanol in chloroform).

Procedure for the Solution Photochemistry of Phosphonate **3**

A solution of phosphonate **3** was prepared in deoxygenated benzene (ca. 0.01 M). The solution was then photolyzed as described earlier. ^{31}P NMR spectroscopy showed that the reaction was complete in about 6 hours with **4** as the exclusive product. The photodimerization product **4** was isolated by HPLC (1.5% methanol in chloroform).

Procedure for Solid-State Photochemistry of Phosphonate **4**

In a Pyrex tube was placed finely powdered phosphonate **3.** The tube was purged well with argon. The powder was irradiated as previously described. The tube was rotated periodically during the irradiation. The reaction was monitored by ^{31}P NMR spectroscopy and was shown to have gone to more than 70% conversion in about 90 hours. The photodimer **4** was isolated by HPLC (1.5% methanol in chloroform).

Preparation of Dichlorodiethylaminophosphine (**7**)

This compound was prepared by a variation on the method of Arbuzov [27], using diethylamine instead of dimethylamine gas. The reaction of diethylamine (84.8 g, 1.16 mol) and phosphorus trichloride (78.5

g, 0.571 mol) in dry ether at −78°C gave the crude material. Distillation resulted in pure **7** (77 g, 0.45 mol, 82%): bp 62–63°C (3 mm Hg) (Ref. [28] 72–75°C, 14 mm Hg). ^{31}P NMR (121 MHz, $CDCl_3$, {^{1}H}) δ 162.45 (Ref. [29] 166).

Preparation of Dimethyl N,N-Diethylphosphoramidite (**8**)

By standard procedures [26], the reaction of **7** (40 g, 0.23 mol) and methyl alcohol (15 g, 0.47 mol) in dry ether at −78°C yielded crude **8.** Distillation afforded pure **8** (24.2 g, 0.145 mol, 62%): bp 65–67°C (10 mm Hg). ^{31}P NMR (121 MHz, $CDCl_3$, {^{1}H}) δ 151.02; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.04 (t, 6H, CH_2CH_3, $^3J_{HH}$ = 8.6 Hz), 3.05 (dq, 4 H, CH_2CH_3, $^3J_{HP}$ = 9.2 Hz, $^3J_{HH}$ = 8.6 Hz), 3.38 (d, 6H, OCH_3, $^3J_{HP}$ = 12.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, {^{1}H}) δ 14.96 (d, $CHCH_3$, $^3J_{CP}$ = 2.9 Hz), 36.91 (d, CH_2CH_3, $^2J_{CP}$ = 20.5 Hz), 50.04 (d, OCH_3, $^2J_{CP}$ = 16.0 Hz).

Preparation of 9-Anthrylmethyl) *Dimethyl Phosphite* (**2**)

The reaction of dimethyl diethylphosphoramidite (2.6 g, 16 mmol) and 9-anthrylmethanol (2.9 g, 14 mmol), followed by flash chromatography (90:5:5 diethyl ether:ethyl acetate:triethylamine), gave **2** as a yellow, thick oil (1.3 g, 4.2 mmol, 30%). ^{31}P NMR (121 MH $CDCl_3$, {^{1}H}) δ 141.81; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.19 (d, 6H, CH_3O, $^3J_{HP}$ = 11.0 Hz), 5.78 (d, 2H, CH_2O, $^3J_{HP}$ = 8.8 Hz), 7.19–7.38 (m, 4H), 7.78 (d, 2H, J = 4.2 Hz), 8.17 (s, 1), 8.49 (d, 2H, J = 4.4 Hz); UV (CH_3CN): 330 (ε 2 × 10^3), 346 (ε 4.1 × 10^3), 360 (ε 8.9 × 10^3), 366 (ε 1.1 × 10^3); GC–EIMS (70 eV) m/z (relative intensity) 300 [M]$^+$ (62), 191 (100); HRMS [M]$^+$ calcd for $C_{17}H_{17}O_3P$: 300.0915; found: 300.0913.

Dimethyl 9-Anthrylmethylphosphonate (**3**)

This compound was isolated from the photolytic mixture of 9-anthrylmethyl dimethyl phosphite (**2**) by HPLC (1.5% methanol in chloroform). Yellow needles, grown by vapor diffusion of pentane into a chloroform solution of **2,** were used for X-ray crystallography: mp 146–149°C. ^{31}P NMR (121 MHz, $CDCl_3$, {^{1}H}) δ 28.23; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.49 (d, 6H, CH_3O, $^3J_{HP}$ = 10.8 Hz), 4.24 (d, 2H, CH_2, $^2J_{HP}$ = 22.6 Hz), 7.46–7.61 (m, 4H), 8.00–8.03 (m, 2H), 8.30–8.33 (m, 2H), 8.43 (d, 1H, J = 3.7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, {^{1}H}) δ 26.43 (d, CH_2, $^1J_{CP}$ = 140.4 Hz), 52.81 (d, CH_3O, $^2J_{CP}$ = 6.9 Hz), 123.15 (d, J_{CP} = 11.2 Hz), 124.71 (d, J_{CP} = 3.5 Hz), 125.03 (d, J_{CP} = 1.9 Hz), 126.17 (d, J_{CP} = 2.1 Hz), 127.42 (d, J_{CP} = 5.9 Hz), 129.10 (d, J_{CP} = 1.9 Hz), 130.44 (d, J_{CP} = 7.0 Hz), 131.48 (d, J_{CP} = 4.3 Hz); UV (CH_3CN): 332 (ε 3.2 × 10^3), 350 (ε 6.8 × 10^3), 368 (ε 1.1 × 10^4), 388 (ε 1.0 × 10^4); GC–EIMS (70 eV) m/z (relative intensity) 300 [M]$^+$ (84), 192 (17), 191 (100), 189 (18). Anal. calcd for $C_{17}H_{17}O_3P$: C, 67.98; H, 5.71. Found: C, 68.06; H, 5.72.

Dianthracene Phosphonate **4**

Photodimer **4** was isolated from the photolytic mixture of the phosphonate monomer **3** by HPLC (1.5% methanol in chloroform). A colorless prism was grown by vapor diffusion of pentane into a chloroform solution of **4**: mp 188–189°C. ^{31}P NMR (121 MHz, $CDCl_3$, {^{1}H}) δ 30.31; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.27 (broad d, 6H, CH_3O, $^3J_{HP}$ = 10.4 Hz), 3.89 (d, 2H, CH_2, $^2J_{HP}$ = 17.4 Hz), 3.95 (s, 1H, bridgehead), 6.83–6.94 (m, 6H), 7.32 (d, 2H, J = 7.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, {^{1}H}) d 36.81 (d, PCH_2, $^2J_{CP}$ = 140.7 Hz), 52.39 (d, CH_3O, $^2J_{CP}$ = 6.9 Hz), 55.58 (d, PCH_2C, $^3J_{CP}$ = 4.8 Hz), 125.42, 125.75 (d, J_{CP} = 5.3 Hz), 127.45, 141.55, 143.03; LR–CIMS (methane) (70 eV) m/z (relative intensity) 601 [M + 1]$^+$ (28), 302 (16), 301 (100), 300 (98), 219 (14), 192 (17), 191 (96). Anal. calcd for $C_{34}H_{34}O_6P_2$: C, 67.98; H, 5.71. Found: C, 67.80; H, 5.69.

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