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Direct Phosphonation of Naphthalene and Phenanthrene with Trialkyl Phosphites via Photochemical Electron Transfer

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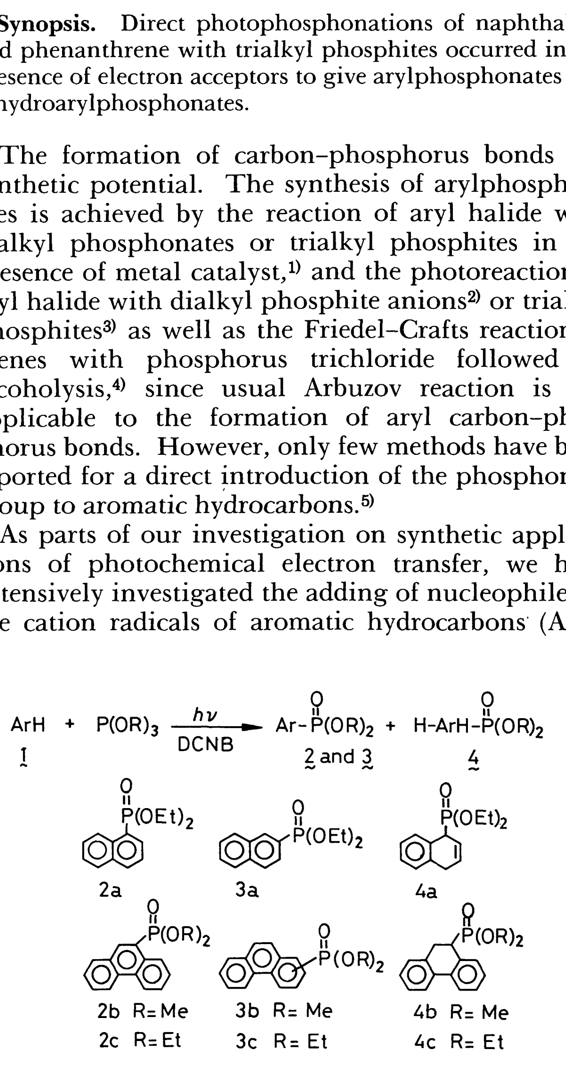
(Received September 14, 1989)

Synopsis. Direct photophosphonations of naphthalene and phenanthrene with trialkyl phosphites occurred in the presence of electron acceptors to give arylphosphonates and dihydroarylphosphonates.

The formation of carbon-phosphorus bonds has synthetic potential. The synthesis of arylphosphonates is achieved by the reaction of aryl halide with dialkyl phosphonates or trialkyl phosphites in the presence of metal catalyst,[1] and the photoreaction of aryl halide with dialkyl phosphite anions[2] or trialkyl phosphites[3] as well as the Friedel–Crafts reaction of arenes with phosphorus trichloride followed by alcoholysis,[4] since usual Arbuzov reaction is not applicable to the formation of aryl carbon–phosphorus bonds. However, only few methods have been reported for a direct introduction of the phosphonate group to aromatic hydrocarbons.[5]

As parts of our investigation on synthetic applications of photochemical electron transfer, we have extensively investigated the adding of nucleophiles to the cation radicals of aromatic hydrocarbons (ArH) generated by photochemical electron transfer to electron acceptors.[6–8] Thus, photochemical electron transfer has proved to be a useful tool for the direct introduction of functional groups, such as cyano and amino groups, to aromatic nuclei.[6,7] From these points of view, we have investigated the direct photophosphonation of naphthalene and phenanthrene with trialkyl phosphites (P(OR)$_3$) in the presence of *m*-dicyanobenzene (DCNB) (Scheme 1).



Scheme 1.

Results and Discussion

Irradiation of an acetonitrile solution containing naphthalene (**1a**), DCNB, and P(OEt)$_3$ under a nitrogen atmosphere by high-pressure mercury lamp gave diethyl 1-naphthylphosphonate (**2a**), diethyl 2-naphthylphosphonate (**3a**), and diethyl (1,4-dihydro-1-naphthyl)phosphonate (**4a**) in 39, 32, and 2% yields, respectively. In the case of phenanthrene (**1b**), diethyl 9-phenanthrylphosphonate (**2b**), the isomer of **2b** (**3b**), and diethyl (9,10-dihydro-9-phenanthryl)phosphonate (**4b**) were obtained in 33, 9, and 13% yields, respectively. The results are shown in Table 1. The arylphosphonates (**2** and **3**) was predominantly formed from a photoreaction in acetonitrile or *N*,*N*-dimethylformamide (DMF) under oxygen or nitrogen atmosphere, while more dihydroarylphosphonates (**4a** and **4b**) were formed in acetonitrile–water (19:1) than in acetonitrile. Moreover, DCNB was substantially consumed to give 1-alkyl-2,4-dicyanobenzenes (**5**) during the photophosphonation of **1b** with P(OR)$_3$ in acetonitrile, whereas high-yield DCNB was recovered in the case of **1a**, as is shown in Table 2.

The photophosphonation was initiated by electron transfer from the excited singlet state of ArH to DCNB to generate the cation radical of ArH (ArH$^{+\cdot}$) and the anion radical of DCNB (DCNB$^{-\cdot}$)(Eq. 1), since the photoreactions were carried out under conditions in

Table 1. Photophosphonation of Arenes with P(OR)$_3$[a)]

Run No.	Arenes	R	Solvent/atmosphere	Products (yield/%)[b)]	Conv. of ArH/%	Recov. of DCNB/%
1	**1a**	Et	CH$_3$CN/N$_2$	**2a** (39) **3a** (32) **4a** (2)	85	64
2	**1a**	Et	CH$_3$CN-H$_2$O(19:1)/N$_2$	**2a** (18) **3a** (32) **4a** (13)	65	72
3	**1b**	Et	CH$_3$CN/N$_2$	**2b** (33) **3b** (9) **4b** (13)	74	32
4	**1b**	Et	CH$_3$CN-H$_2$O(19:1)/N$_2$	**2b** (12) **3b** (14) **4b** (52)	84	76
5	**1b**	Me	CH$_3$CN/O$_2$	**2c** (58) **3c** (17) **4c** (20)	96	78
6	**1b**	Me	DMF/O$_2$	**2c** (52) **3c** (7) **4c** (4)	88	80

a) See text. b) Isolated yields based on arene used.

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Table 2. The Formation of 1-Alkyl-2,4-dicyanobenzene (**5**) from the Photoreaction of **1b** with $P(OR)_3$ in the Presence of DCNB[a)]

Run No.	R	Irradn. time/h	Products (yield/%)[b)]	Conv. of DCNB/%	Recov. of **1b**/%
1	Me	70	**5a** (15)	15	43
2	Et	58	**5b** (62)	80	50
3[c)]	Et	60	**5b** (0)	8	—
4	*i*-Pr	55	**5c** (32)	82	13

a) For 100 ml of acetonitrile solution containing DCNB (5 mmol), $P(OR)_3$ (50 mmol), and **1b** (5 mmol). b) Isolated yields based on DCNB used. c) In the absence of **1b**.

which the fluorescence of **1a** or **1b** was exclusively quenched by DCNB, but negligibly by $P(OR)_3$. Notable observations of mechanistic significance are i) less regioselective compared with photoamination by amines and photocyanation by cyanide anion,[6,7)] ii) the close oxidation potentials of $P(OR)_3$ to that of ArH, i.e. $E^{ox}_{1/2}(P(OEt)_3)=1.25$, $E^{ox}_{1/2}(\mathbf{1a})=1.22$,[8)] and $E^{ox}_{1/2}(\mathbf{1b})=1.17$ eV,[8)] and iii) a considerable consumption of DCNB.

$$\mathrm{ArH} + \mathrm{DCNB} \xrightarrow{h\nu} \mathrm{ArH}^{+\cdot} + \mathrm{DCNB}^{-\cdot} \qquad (1)$$

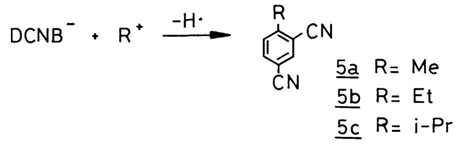
$$\mathrm{ArH}^{+\cdot} + \mathrm{P(OR)_3} \longrightarrow \mathrm{ArH} + \mathrm{P(OR)_3^{+\cdot}} \qquad (2)$$

$$\mathrm{P(OR)_3^{+\cdot}} \longrightarrow \cdot\mathrm{P(O)(OR)_2} + \mathrm{R^+} \qquad (3)$$

$$\mathrm{ArH} + \cdot\mathrm{P(O)(OR)_2} \longrightarrow \cdot\mathrm{ArH\text{-}P(O)(OR)_2} \qquad (4)$$

$$\cdot\mathrm{ArH\text{-}P(O)(OR)_2} \xrightarrow{\text{oxid./-H}^+} \underline{2} \text{ or } \underline{3} \qquad (5)$$

$$\cdot\mathrm{ArH\text{-}P(O)(OR)_2} \xrightarrow{\mathrm{DCNB}^{-\cdot}/\mathrm{H}^+} \underline{4} \qquad (6)$$



(7)

5a R= Me
5b R= Et
5c R= i-Pr

It has been reported that the nucleophiles, such as cyanide anion and amines, added selectively at C1 of $\mathbf{1a}^{+\cdot}$ or at C9 of $\mathbf{1b}^{+\cdot}$, where the highest positive charge might develop.[6b,7)] However, photophosphonation is too less-regioselective to proceed only by a nucleophilic addition of $P(OR)_3$ to $ArH^{+\cdot}$. Previous studies on photoamination showed that the dialkylamines of the oxidation potentials close to that of ArH undergo an electron exchange with $ArH^{+\cdot}$ in competition with nucleophilic addition.[6b)] From the above observations, it is, therefore, strongly suggested that the electron exchange between $P(OR)_3$ and $ArH^{+\cdot}$ occurs to generate $P(OR)_3^{+\cdot}$ which would decompose to the dialkoxyphosphoryl radicals ($\cdot P(O)(OR)_2$) and carbocation (Eqs. 2 and 3). The less regioselective phosphonation can be attributed to the addition of the $\cdot P(O)(OR)_2$ to ArH, as is shown in Eqs. 4—6. The resulting phosphorylaryl radicals become fully aromatic (**2** and **3**) upon oxidation followed by deprotonation and/or are reduced with $DCNB^{-\cdot}$ followed by protonation to give **4**. A similar mechanism has been reported for the free-radical phosphonation by $\cdot P(O)(OR)_2$, generated from diethyl phosphonate and *t*-butyl peroxide.[5)] Moreover, the formation of **5** would arise from the reaction of $DCNB^{-\cdot}$ with carbocation generated from $P(OR)_3^{+\cdot}$ (Eq. 7).

Experimental

The ^1H and ^{13}C NMR spectra were taken on a JEOL JNM60 and a JEOL FX 90 spectrometer, respectively, for a $CDCl_3$ solution using tetramethylsilane as the internal standard. Gas chromatography was performed on a Shimadzu GC-8A using a 50 cm column of 2% OV-17 on Chromosorb W. The fluorescence quenching experiments were performed for a degassed acetonitrile solution on a Hitachi MPF-4 spectrometer. Mass spectra were measured on a JEOL D-300S equipped with a JMA 2000 data analyzer. Measurements of oxidation potentials were performed for deaerated acetonitrile solutions containing $P(OEt)_3$ (1×10^{-3} mol dm^{-3}) and a supporting electrolyte, tetraethyl ammonium tetrafluoroborate (0.1 mol dm^{-3}), vs. Ag/AgNO$_3$ of reference electrode at 23±0.1 °C by a Hokuto Denko HA-501G potentiostat and a Hokuto Denko HB-105 voltage generator.

Photoreactions of Arenes. Irradiation was performed for a solution (100 ml) containing an arene (10 mmol), *m*-dicyanobenzene (5 mmol), and a trialkyl phosphite (50 mmol) by a high-pressure Hg lamp under cooling with water. After evaporation under reduced pressure, the photolysates were dissolved in 100 ml of benzene and then extracted with 50 ml of water. The benzene solution was chromatographed on silica gel with hexane, benzene, and ethyl acetate as the eluents; the products were thus isolated. The structure of **2a** or **2b** was determined by comparisons with authentic samples prepared from the reaction of 1-bromonaphthalene or 9-bromophenanthrene with sodium diethyl phosphite in the presence of cupper(I) iodide. Although the structures of **3b** and **3c** could not unambiguously be determined, they were reduced to be 1-phenanthrylphosphonates from the ^1H NMR spectra. **4a**—**c** could not be purified by rapid aromatization to **1a** or **1b** during purification.

Diethyl 1-Naphthylphosphonate (2a). ^1H NMR $\delta=1.31$ (t, $J=7$ Hz, 6H), 4.14 (dq, $J=7$ and 12 Hz, 4H), 7.46—7.69 (m, 3H), 7.86—8.58 (m, 4H), ^{13}C NMR $\delta=16.3$ (d, $J=6$ Hz), 62.2 (d, $J=6$ Hz), 124.2, 124.8, 126.3, 126.7 (d, $J=3$ Hz), 127.4, 128.7, 128.8, 133.6 (d, $J=3$ Hz), 133.9, 134.6 (d, $J=9$ Hz), MS *m/z* 264 (M$^+$), 235, 190, 155, 138.

Diethyl 2-Naphthylphosphonate (3a). ^1H NMR $\delta=1.35$ (t, $J=7$ Hz, 6H), 4.15 (dq, $J=7$ and 11 Hz, 4H), 7.5—8.0 (m, 6H), 8.42 (d, $J=15$ Hz, 1H). ^{13}C NMR $\delta=16.4$ (d, $J=6$ Hz), 62.2 (d, $J=5$ Hz), 126.5 (d, $J=11$ Hz), 126.9, 127.8, 128.0, 128.2, 128.8 (d, $J=7$ Hz), 129.0, 132.1, 132.8, 134.1 (d, $J=10$ Hz), MS *m/z* 264, IR 1230 cm^{-1}.

Diethyl (1,4-Dihydro-1-naphthyl)phosphonate (4a). ^1H NMR $\delta=1.2$ and 1.3 (t, $J=7$ Hz, 6H), 3.4 (m, 2H), 3.8 (dq, $J=7$ and 12 Hz, 4H), 4.1 (m, 1H), 5.9—6.0 (m, 2H), 7.0—7.1 (m, 3H), 7.2—7.25 (m, 1H), MS *m/z* 266 (M$^+$), 128, IR 1230 cm^{-1}.

Diethyl 9-Phenanthrylphosphonate (2b). ^{1}H NMR δ=1.3 (t, J=7 Hz, 6H), 4.0 (dq, J=7 and 11 Hz, 4H), 7.6—7.7 (m, 4H), 8.0 (d, J=8.1 Hz, 1H), 8.5—8.7 (m, 4H), ^{13}C NMR δ=16.4 (d, J=6 Hz), 62.3 (d, J=5 Hz), 122.6, 123.0 (d, J=1 Hz), 127.0, 127.2, 127.2, 127.6 (d, J=3 Hz), 129.2, 129.8 (d, J=4 Hz), 130.0, 130.0, 130.5, 130.7, 132.3, (d, J=3 Hz), 138.2 (d, J=9 Hz), MS m/z 314 (M^{+}), 205, 178, IR 1250 cm^{-1}.

Isomer of 2b (3b). ^{1}H NMR δ=1.3 (t, J=7 Hz, 6H), 4.0 (dq, J=7 Hz, 4H), 7.3—7.8 (m, 7H), 8.5—8.7 (m, 1H), 9.0 (d, J=16 Hz, 1H), ^{13}C NMR δ=16.3 (d, J=6 Hz), 62.1 (d, J=5 Hz), 122.5, 122.9, 126.2, 127.1, 127.8 (d, J=7 Hz), 128.0 (d, J=5 Hz), 128.4 (d, J=3 Hz), 128.6, 128.9, 129.4, 130.0, 131.5, 132.1 (d, J=3 Hz), 134.3 (d, J=9 Hz), MS m/z 314 (M^{+}), 286, 258, 240, 205, 178, IR 1230 cm^{-1}.

Diethyl (9,10-Dihydro-9-phenanthryl)phosphonate (4b). ^{1}H NMR δ=1.2—1.3 (t, J=7 Hz, 6H), 2.8—3.2 (m, 2H), 3.3—3.4 (m, 1H), 3.8 (dt, J=7 and 9 Hz, 4H), 7.0—7.2 (m, 6H), 7.46—7.7 (m, 2H), MS m/z 316 (M^{+}), 206, 178, IR 1250 cm^{-1}.

Dimethyl 9-Phenanthrylphosphonate (2c). ^{1}H NMR δ= 3.82 (d, J=11.5 Hz, 6H), 7.6—7.8 (m, 4H), 7.9—8.1 (m, 1H), 8.4—8.8 (m, 4H), MS m/z 286 (M^{+}), 191, 178.

Isomer of 2c (3c). ^{1}H NMR δ=3.69 (d, J=11 Hz, 6H), 7.54—7.67 (m, 3H), 7.74—7.86 (m, 4H), 8.77 (d, J=8.2 Hz, 1H), 9.13 (d, J=14 Hz, 1H), MS m/z 286 (M^{+}), 191, 178, IR 1250 cm^{-1}.

Dimethyl (9,10-Dihydro-9-phenanthryl)phosphonate (4c). ^{1}H NMR δ=3.0—3.95 (m, 2H), 3.03 and 3.36 (d, J=10 Hz, 6H), 3.4—3.6 (m, 1H), 7.03—7.23 (m, 6H), 7.47—7.67 (m, 2H), MS m/z 288 (M^{+}), 178, IR 1250 cm^{-1}.

The spectral data of 1-methyl and 1-ethyl-2,4-dicyanobenzenes (**5a**, **b**) have been reported;[6a] **5b**, mp 66—67 °C.

1-Isopropyl-2,4-dicyanobenzene (5c). mp 78—79 °C, ^{1}H NMR δ=1.30 (d, J=6 Hz, 6H), 3.30 (sept, J=6 Hz, 1H), 7.13 (d, J=8 Hz, 1H), 7.43 (d, J=8 Hz, 1H), 7.50 (s, 1H), MS m/z 170, IR 2240 cm^{-1}.

This research was supported by a Grand-in-Aid for Scientific Research from the Ministry of Education, Science and Culture (No. 01750789).

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