

# Cyanide Ion Promoted Addition of Acylphosphonates to Diethyl Cyanophosphonate: Synthesis of Phosphonocyanohydrin *O*-Phosphates

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**Abstract:** Cyanide ion catalyzed addition of acylphosphonates to diethyl cyanophosphonate furnished phosphonocyanohydrin *O*-phosphates in high yield. The reaction works via the phosphonate–phosphate rearrangement, followed by the addition of diethyl cyanophosphonate to the cyanohydrin phosphate anion.

**Key words:** phosphonocyanohydrins, diethyl cyanophosphonate, addition reactions, acyl phosphonates, nucleophilic additions

Cyanohydrins and their trimethylsilyl ethers are versatile intermediates in organic synthesis.<sup>1,2</sup> Many methods have been devised for the synthesis of these target compounds in a racemic and enantioselective manner. The typical method for their synthesis is the addition of a cyanide source, in various forms, to the corresponding carbonyl compounds.<sup>3</sup> The source of cyanide determines the respective type of the protecting group on hydroxy functionality, which is, most of the time, crucial for the success of subsequent transformations. Since the instability of cyanohydrins and their trimethylsilyl ethers is sometimes problematic for further transformations, the development of a one-pot cyanation–*O*-protection reaction with a stable protecting group has become desirable.<sup>4</sup> In 1983, the one-pot reaction of carbonyl compounds with diethyl cyanophosphonate (DEPC) in the presence of lithium diisopropylamide was reported by Harusawa et al.<sup>5</sup> Subsequently, several catalytic asymmetric cyano-phosphorylation methods were developed for aldehydes and prochiral ketones.<sup>6</sup> Recently, Baeza et al. reported a catalytic asymmetric cyano-phosphorylation reaction using a chiral aluminum catalyst<sup>7</sup> with diethyl cyanophosphonate, which is revealed as an excellent phosphorylating agent in the asymmetric processes. There are several methods for the transformation of aldehydes and ketones into racemic cyanohydrin *O*-phosphates by their reaction with diethyl cyanophosphonate.<sup>8</sup> In our work, we applied the known reaction of diethyl cyanophosphonate with carbonyls to acylphosphonates.

In recent years, we have published several papers on the addition reactions of acylphosphonates.<sup>9</sup> There are also some publications related to the synthesis and reactions of acylphosphonates in order to form phosphonocyanohy-

drins and their rearrangement to cyanohydrin phosphates.<sup>10</sup>

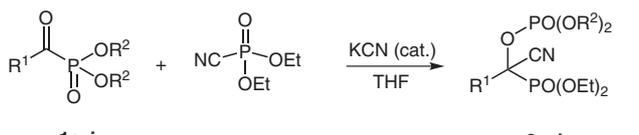
In the present paper, we report the cyano-phosphorylation of various alkyl and aryl phosphonates by their reaction with stoichiometric amounts of diethyl cyanophosphonate and substoichiometric amounts of potassium cyanide. The products can be further converted into various interesting structures, such as functionalized amino phosphonic acids and carboxylic acid derivatives.

For the investigation of the reaction of the diethyl cyanophosphonate with acylphosphonates **1**, we planned to gain direct and uncatalyzed access to phosphonocyanohydrin *O*-phosphates **2** by using diethyl cyanophosphonate both as a cyanide source and as an electrophile. Moreover, we hoped that diethyl cyanophosphonate could supply a catalytic amount of cyanide ion by decomposition in order to provide cyanohydrin phosphate, which can subsequently start the reaction. The formation of cyanohydrin phosphate, via phosphonate–phosphate rearrangement, and followed by C-phosphonylation, should in turn form phosphonocyanohydrin *O*-phosphates.

In the first reaction, dimethyl benzoylphosphonate (**1e**) was reacted with diethyl cyanophosphonate at ambient temperature in diethyl ether and monitored by TLC; no product formation was observed. However, in the presence of catalytic quantities of potassium cyanide, benzoylphosphonate **1e** reacted slowly with diethyl cyanophosphonate in diethyl ether to afford the desired product **2e** in a very low yield. The reaction was repeated with various solvents and at various temperatures (data not shown) and the best result was obtained with tetrahydrofuran.

When benzoylphosphonate **1e** was reacted with diethyl cyanophosphonate in the presence of catalytic quantities of potassium cyanide in tetrahydrofuran, the desired (cyano)(diethoxyphosphoryl)(phenyl)methyl dimethyl phosphate (**2e**) was obtained in 90% yield after purification by column chromatography (Table 1, entry 5). The reaction scope was studied using a variety of acylphosphonates and the corresponding cyanohydrin *O*-phosphates were synthesized in good to high yields (Table 1).

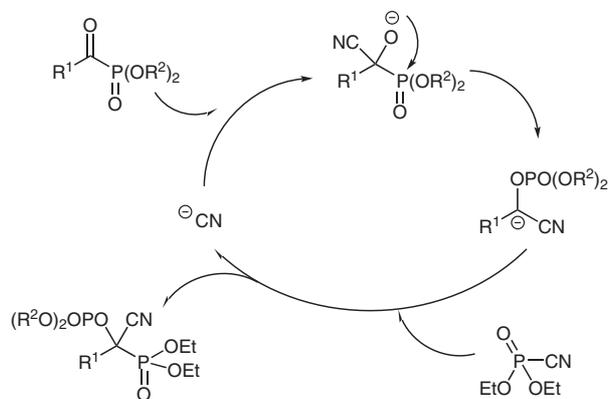
From the obtained products, only one compound of this class **2a** has been synthesized before in the reaction of acetyl cyanide with pyrophosphites.<sup>11</sup> Similar compounds were also described by Gazizov et al.<sup>12</sup> and Pudovik.<sup>13</sup>

**Table 1** Addition of Acylphosphonates to Diethyl Cyanophosphate<sup>a</sup>


Entry	R <sup>1</sup>	R <sup>2</sup>	Product	Yield (%)
1	Me	Me	<b>2a</b>	75
2	Et	Me	<b>2b</b>	73
3	<i>t</i> -Bu	Me	<b>2c</b>	81
4	Cy	Me	<b>2d</b>	85
5	Ph	Me	<b>2e</b>	90
6	4-MeC <sub>6</sub> H <sub>4</sub>	Me	<b>2f</b>	86
7	4-MeOC <sub>6</sub> H <sub>4</sub>	Me	<b>2g</b>	82
8	4-FC <sub>6</sub> H <sub>4</sub>	Me	<b>2h</b>	80
9	4-MeC <sub>6</sub> H <sub>4</sub>	Me	<b>2i</b>	86
10	Ph	Et	<b>2j</b>	88

<sup>a</sup> Reaction conditions: **1a–j** (1 mmol), DEPC (1 mmol), KCN (cat.), THF, r.t., 12–24 h.

Presumably, the addition of the cyanide ion to the acylphosphonate forms the intermediate alkoxide, which rearranges to the carbanion that in turn reacts with diethyl cyanophosphate in order to provide the product. The proposed catalytic cycle is outlined in Scheme 1.

**Scheme 1**

In conclusion, we have developed a convenient, one-pot procedure for preparing various polyfunctionalized cyanoaldehydes with the formation of a new C–P bond starting from readily available acylphosphonates and diethyl cyanophosphate under mild conditions in good to high yields (73–90%). The general applicability of the reaction with a range of acylphosphonate and diethyl cyanophosphate was demonstrated.

All reactions were carried out in oven-dried Schlenk tubes with magnetic stirring under a positive pressure of argon. Solvents were freshly distilled under an argon atmosphere prior to use. Carboxylic acids, trialkylphosphites and DEPC were purchased from Aldrich and used as received. Acyl phosphonates were prepared according to the literature procedures and purified by vacuum distillation.<sup>9</sup> Thin-layer chromatography (TLC) was conducted on aluminum sheets that were pre-coated with silica gel SIL G/UV254 from MN GmbH & Co.; spots were visualized using UV light (254 nm) and/or by staining with ninhydrin. Chromatographic separations were performed using silica gel (MN-silica gel 60, 230–400 mesh). IR measurements were performed on a Varian 1000 FTIR spectrophotometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker DPX400 NMR spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) relative to the residual protons in the NMR solvent (<sup>1</sup>H NMR: CHCl<sub>3</sub>, δ = 7.24 ppm) and carbon resonance of the solvent (<sup>13</sup>C NMR: CDCl<sub>3</sub>, δ = 77.0 ppm). Elemental analyses were performed using a LECO CHNS-932 instrument.

### 1-(Alkoxyphosphoryl)-1-cyanoalkyl Dialkyl Phosphates **2a–j**; General Procedure

To a soln of acylphosphonate **1a–j** (1 mmol) in anhyd THF (2 mL) was added DEPC (1.52 mL, 1 mmol) under argon at r.t. Then, KCN (2 mg) was added in one portion. The reaction was stirred at r.t. and monitored by TLC (completed within 12–24 h). After the reaction reached completion, THF was removed under reduced pressure and the crude product was purified by flash column chromatography (EtOAc).

#### 1-Cyano-1-(diethoxyphosphoryl)ethyl Dimethyl Phosphate (**2a**)

Yellow oil; yield: 75%.

IR (KBr): 2990, 2256, 1435, 1270, 1028, 845, 590 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 1.33 (m, 6 H), 1.97 (d, *J* = 14.7 Hz, 3 H), 3.89 (d, *J* = 6.5 Hz, 3 H), 3.92 (d, *J* = 6.5 Hz, 3 H), 4.07–4.21 (m, 4 H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 115.3, 69.6 (dd, *J* = 178.7, 9.3 Hz), 64.8 (d, *J* = 6.0 Hz), 64.6 (d, *J* = 6.0 Hz), 55.7 (d, *J* = 6.3 Hz), 55.1 (d, *J* = 6.5 Hz), 22.1, 16.0 (d, *J* = 6.7 Hz).

<sup>31</sup>P NMR (CDCl<sub>3</sub>): δ = -5.3 (d, *J* = 32 Hz), 13.1 (d, *J* = 32 Hz).

Anal. Calcd for C<sub>9</sub>H<sub>19</sub>NO<sub>7</sub>P<sub>2</sub> (315.06): C, 34.29; H, 6.08; N, 4.44. Found: C, 34.43; H, 6.25; N, 4.29.

#### 1-Cyano-1-(diethoxyphosphoryl)propyl Dimethyl Phosphate (**2b**)

Yellow oil; yield: 73%.

IR (KBr): 2985, 2240, 1470, 1375, 1281, 1027, 835, 559 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 1.16 (t, *J* = 7.6 Hz, 3 H), 1.33 (m, 6 H), 2.27 (m, 2 H), 3.89 (d, *J* = 2.9 Hz, 3 H), 3.91 (d, *J* = 2.9 Hz, 3 H), 4.16 (m, 4 H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 114.2, 73.9 (dd, *J* = 175.4, 9.9 Hz), 64.7 (d, *J* = 6.1 Hz), 64.6 (d, *J* = 6.1 Hz), 55.5 (d, *J* = 7.0 Hz), 55.0 (d, *J* = 7.2 Hz), 29.7, 16.0 (d, *J* = 6.8 Hz), 8.42 (d, *J* = 5.2 Hz).

<sup>31</sup>P NMR (CDCl<sub>3</sub>): δ = -5.0 (d, *J* = 32 Hz), 13.2 (d, *J* = 32 Hz).

Anal. Calcd for C<sub>10</sub>H<sub>21</sub>NO<sub>7</sub>P<sub>2</sub> (329.22): C, 36.48; H, 6.43; N, 4.25. Found: C, 36.35; H, 6.61; N, 4.14.

#### 1-Cyano-1-(diethoxyphosphoryl)-2,2-dimethylpropyl Dimethyl Phosphate (**2c**)

Yellow oil; yield: 81%.

IR (KBr): 2983, 2245, 1479, 1372, 1275, 1031, 837, 589 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 1.21 (s, 9 H), 1.33 (t, *J* = 7.0 Hz, 6 H), 3.88 (d, *J* = 10.9 Hz, 3 H), 3.92 (d, *J* = 10.9 Hz, 3 H), 4.13–4.21 (m, 4 H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 114.0, 79.7$  (dd,  $J = 169.3, 12.9$  Hz), 64.7 (d,  $J = 5.8$  Hz), 55.2 (d,  $J = 7.5$  Hz), 55.1 (d,  $J = 7.0$  Hz), 40.9, 25.8, 16.0.

$^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ):  $\delta = -5.8$  (d,  $J = 16$  Hz), 12.6 (d,  $J = 16$  Hz).

Anal. Calcd for  $\text{C}_{12}\text{H}_{25}\text{NO}_7\text{P}_2$  (357.28): C, 40.34; H, 7.05; N, 3.92. Found: C, 39.65; H, 7.19; N, 4.16.

**(Cyano)(cyclohexyl)(diethoxyphosphoryl)methyl Dimethyl Phosphate (2d)**

Yellow oil; yield: 85%.

IR (KBr): 2987, 2254, 1449, 1270, 1046, 808, 764  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.17\text{--}1.35$  (m, 12 H), 1.62–2.18 (m, 5 H), 3.88 (d,  $J = 3.8$  Hz, 3 H), 3.91 (d,  $J = 3.9$  Hz, 3 H), 4.12–4.20 (m, 4 H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 114.0, 76.7$  (dd,  $J = 171.7, 11.7$  Hz), 64.7 (d,  $J = 5.3$  Hz), 63.4 (d,  $J = 5.5$  Hz), 55.5 (d,  $J = 7.4$  Hz), 55.1 (d,  $J = 7.3$  Hz), 44.8, 27.3 (dd,  $J = 16.7, 3.6$  Hz), 25.9, 25.6, 16.0 (m).

$^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ):  $\delta = -5.2$  (d,  $J = 32$  Hz), 12.8 (d,  $J = 32$  Hz).

Anal. Calcd for  $\text{C}_{14}\text{H}_{27}\text{NO}_7\text{P}_2$  (383.31): C, 43.87; H, 7.10; N, 3.65. Found: C, 43.70; H, 7.21; N, 3.87.

**(Cyano)(diethoxyphosphoryl)(phenyl)methyl Dimethyl Phosphate (2e)**

Colorless oil; yield: 90%.

IR (KBr): 2986, 2256, 1443, 1273, 1028, 847, 808  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.19$  (t,  $J = 7.0$  Hz, 3 H), 1.24 (t,  $J = 7.2$  Hz, 3 H), 3.60 (d,  $J = 10.8$  Hz, 3 H), 3.87 (d,  $J = 10.8$  Hz, 3 H), 3.94–4.10 (m, 4 H), 7.40 (m, 3 H), 7.70 (m, 2 H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 130.9, 130.2, 128.6, 127.2, 114.2, 75.0$  (dd,  $J = 172.4, 11.0$  Hz), 64.7 (d,  $J = 5.9$  Hz), 64.5 (d,  $J = 5.9$  Hz), 55.9 (d,  $J = 6.9$  Hz), 55.7 (d,  $J = 7.1$  Hz), 15.7 (m).

$^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ):  $\delta = -4.7$  (d,  $J = 48$  Hz), 11.6 (d,  $J = 48$  Hz).

Anal. Calcd for  $\text{C}_{14}\text{H}_{21}\text{NO}_7\text{P}_2$  (377.27): C, 44.57; H, 5.61; N, 3.71. Found: C, 44.70; H, 5.75; N, 3.89.

**(Cyano)(diethoxyphosphoryl)(*p*-tolyl)methyl Dimethyl Phosphate (2f)**

Colorless oil; yield: 86%.

IR (KBr): 2986, 2260, 1446, 1274, 1020, 859, 763  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.20$  (m, 6 H), 2.33 (s, 3 H), 3.59 (d,  $J = 10.8$  Hz, 3 H), 3.87 (d,  $J = 10.8$  Hz, 3 H), 3.93–4.10 (m, 4 H), 7.18 (d,  $J = 8.1$  Hz, 2 H), 7.57 (dd,  $J = 8.2, 1.8$  Hz, 2 H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 140.4, 129.3, 127.8, 127.3, 114.3, 75.1$  (dd,  $J = 178.0, 10.8$  Hz), 64.7 (d,  $J = 5.9$  Hz), 64.5 (d,  $J = 5.9$  Hz), 55.9 (d,  $J = 6.9$  Hz), 55.6 (d,  $J = 6.9$  Hz), 21.2, 15.8 (m).

$^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ):  $\delta = -4.7$  (d,  $J = 48$  Hz), 11.7 (d,  $J = 48$  Hz).

Anal. Calcd for  $\text{C}_{15}\text{H}_{23}\text{NO}_7\text{P}_2$  (391.29): C, 46.04; H, 5.92; N, 3.58. Found: C, 46.27; H, 5.75; N, 3.78.

**(Cyano)(diethoxyphosphoryl)(4-methoxyphenyl)methyl Dimethyl Phosphate (2g)**

Colorless oil; yield: 82%.

IR (KBr): 2978, 2247, 1435, 1270, 1018, 850, 785  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.24$  (m, 6 H), 3.58 (d,  $J = 10.8$  Hz, 3 H), 3.76 (s, 3 H), 3.88 (d,  $J = 10.6$  Hz, 3 H), 3.92–4.09 (m, 4 H), 6.88 (d,  $J = 8.6$  Hz, 2 H), 7.60 (d,  $J = 8.5$  Hz, 2 H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 161.1, 129.0$  (d,  $J = 4.5$  Hz), 122.4, 114.4, 113.9, 74.8 (dd,  $J = 187.0, 11.7$  Hz), 64.6 (d,  $J = 6.1$

Hz), 64.4 (d,  $J = 5.9$  Hz), 55.8 (d,  $J = 7.6$  Hz), 55.5 (d,  $J = 7.3$  Hz), 55.2, 16.0 (d,  $J = 6.4$  Hz).

$^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ):  $\delta = -5.3$  (d,  $J = 48$  Hz), 11.3 (d,  $J = 48$  Hz).

Anal. Calcd for  $\text{C}_{15}\text{H}_{23}\text{NO}_8\text{P}_2$  (407.29): C, 44.23; H, 5.69; N, 3.44. Found: C, 44.35; H, 5.81; N, 3.55.

**(Cyano)(diethoxyphosphoryl)(4-fluorophenyl)methyl Dimethyl Phosphate (2h)**

Colorless oil; yield: 80%.

IR (KBr): 2990, 2260, 1465, 1284, 1048, 875  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.23$  (m, 6 H), 3.63 (d,  $J = 10.7$  Hz, 3 H), 3.90 (d,  $J = 10.8$  Hz, 3 H), 3.96–4.11 (m, 4 H), 7.08 (t,  $J = 8.5$  Hz, 2 H), 7.70 (m, 2 H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 163.7$  (d,  $J = 250$  Hz), 129.7, 126.8, 115.7, 114.0, 74.4 (dd,  $J = 173.5, 10.8$  Hz), 64.8 (d,  $J = 5.9$  Hz), 64.6 (d,  $J = 6.0$  Hz), 56.0 (d,  $J = 6.9$  Hz), 55.7 (d,  $J = 7.0$  Hz), 15.8 (m).

$^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ):  $\delta = -5.2$  (d,  $J = 49$  Hz), 10.9 (d,  $J = 49$  Hz).

Anal. Calcd for  $\text{C}_{14}\text{H}_{20}\text{FNO}_7\text{P}_2$  (395.26): C, 42.54; H, 5.10; F, 4.81; N, 3.54. Found: C, 43.15; H, 5.34; F, 4.65; N, 3.23.

**(Cyano)(diethoxyphosphoryl)(*m*-tolyl)methyl Dimethyl Phosphate (2i)**

Yellow oil; yield: 86%.

IR (KBr): 2987, 2260, 1446, 1280, 1050, 855  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.23$  (m, 6 H), 2.35 (s, 3 H), 3.60 (d,  $J = 2.9$  Hz, 3 H), 3.86 (d,  $J = 3.0$  Hz, 3 H), 3.90–4.10 (m, 4 H), 7.23 (m, 1 H), 7.28 (m, 1 H), 7.50 (m, 2 H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 137.3, 130.0, 129.6, 127.4, 126.7, 123.3, 113.2, 74.1$  (dd,  $J = 173.6, 11.1$  Hz), 63.6 (d,  $J = 5.6$  Hz), 63.4 (d,  $J = 5.9$  Hz), 54.9 (d,  $J = 7.0$  Hz), 54.6 (d,  $J = 7.9$  Hz), 20.4, 14.7 (m).

$^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ):  $\delta = -4.7$  (d,  $J = 38$  Hz), 11.7 (d,  $J = 38$  Hz).

Anal. Calcd for  $\text{C}_{15}\text{H}_{23}\text{NO}_7\text{P}_2$  (391.29): C, 46.04; H, 5.92; N, 3.58. Found: C, 46.27; H, 5.75; N, 3.78.

**Cyano(diethoxyphosphoryl)(phenyl)methyl Diethyl Phosphate (2j)**

Yellow oil; yield: 88%.

IR (KBr): 2991, 2268, 1454, 1290  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.23$  (m, 12 H), 3.73–4.34 (m, 8 H), 7.39 (m, 3 H), 7.69 (m, 2 H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 131.1, 130.2, 128.5, 127.5, 114.5, 74.5$  (dd,  $J = 172.4, 11.0$  Hz), 65.8 (d,  $J = 5.9$  Hz), 64.6 (d,  $J = 5.9$  Hz), 16.0 (m).

$^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ):  $\delta = -4.7$  (d,  $J = 48$  Hz), 9.30 (d,  $J = 48$  Hz).

Anal. Calcd for  $\text{C}_{16}\text{H}_{25}\text{NO}_7\text{P}_2$  (405.32): C, 47.41; H, 6.22; N, 3.46. Found: C, 47.50; H, 6.23; N, 3.49.

**Supporting Information** for this article is available online at <http://www.thieme-connect.com/ejournals/toc/synthesis>.

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