A Convenient synthesis of 1-(diethoxyphosphoryl)cyclopropanecarboxylates

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Abstract

An efficient synthesis of a series of 1-(diethoxyphosphoryl)cyclopropanecarboxylates was accomplished by the reaction of terminal 1,2-diols cyclic sulfates with triethylphosphonoacetate. The stereochemistry of 2-benzyloxymethyl-1-(diethoxyphosphoryl)cyclopropanecarboxylic acid was determined by the single crystal X-ray structure analysis.

Keywords: Cyclopropanation, cyclopropanecarboxylates, 2,2-dioxo-1,3,2-dioxathiolanes, 1-(diethoxyphosphoryl)cyclopropanecarboxylates, X-ray analysis

Introduction

During the last several years cyclopropanation of dialkyl malonates with 4-alkyl-2,2-dioxo-1,3,2-dioxathiolanes has emerged as a versatile method for construction of cyclopropane carboxylic acid derivatives - the attractive synthons of aminocyclopropanecarboxylic acids and various carbo- and heterocyclic compounds.¹⁻⁸ It is well documented that succeeding steps of this reaction consist in fully regioselective dioxathiolane ring opening with the malonate anion and intramolecular S_N2 type substitution of a sulfate residue in the resulting intermediate. Surprisingly, similar cyclopropanation of acetates activated by other electron withdrawing groups remains almost unexplored. To the best of our knowledge the literature contains only one example of such a reaction. It has been demonstrated that the base promoted cyclopropanation of *t*-butyl dimethoxyphosphorylacetate with (*S*)-4-methyl-2,2-dioxo-1,3,2-dioxathiolane proceeds highly regio- and stereoselective, affording *t*-butyl *trans*-(1*R*,2*R*)-1-dimethoxyphosphoryl-2-methylcyclopropanecarboxylate with *ee*>99% and *de* 94%.⁹

170(3) (°); atom indicated with an asterisk is related by the (x, y-1, z) symmetry operator] resulting in a ladder type arrangement extending along the [010] crystallographic axis. The crystal packing is additionally stabilized by the C-H $\cdots\pi$ interactions¹⁶ between the phenyl rings and hydrogen atoms of the methylene groups. Therefore, taking into account the method of preparation and structural similarity, we by analogy assigned the *trans* configuration to the obtained products **4a-d**. In this context, it is also worth nothing that the values of coupling constant $^3J_{\text{PH}} = 16.0$ Hz and $^3J_{\text{PH}} = 16.5$ Hz observed in ^1H NMR spectra of **4a** and **5** respectively, were consistent with the synperiplanar arrangement of the phosphorus and H-2 atoms.

Figure 1. The molecular structure and numbering scheme of the cyclopropane carboxylic acid **5**. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are represented by circles of an arbitrary radius. Selected bond lengths [Å]: P-O3 1.466(2); P-C1 1.787(3); O1-C12 1.197(3); O2-C12 1.312(4); O6-C4 1.417(4); C1-C3 1.521(4); C1-C2 1.554(3); C2-C3 1.472(5); C1-C12 1.492(4); C2-C4 1.493(4). Selected valency angles [°]: P-C1-C2 112.6(2); P-C1-C3 116.1(2); P-C1-C12 121.5(2); C1-C2-C3 60.3(2); C1-C3-C2 62.5(2); C2-C1-C3 57.2(2); C1-C2-C4 122.9(2); C3-C2-C4 123.9(3); C2-C1-C12 117.7(2) C3-C1-C12 115.2(2);. Selected torsion angles [°]: P-C1-C2-C3 107.4(2); P-C1-C2-C4 -139.3(3); P-C1-C12-O2 13.9(3); O1-C12-C1-C3 -17.7(4); O3-P-C1-C2 -32.7(2) ; O3-P-C1-C3 30.6(3); O3-P-C2-C12 179.6(2); O6-C4-C3-C1 170.3(3); C4-C3-C2-C12 9.8(4).

Scheme 2

Conclusions

In summary, our studies have clearly demonstrated general applicability of synthetic strategy based on cyclopropanation of triethylphosphonoacetate **3** with cyclic sulfates **2** of terminal 1,2-diols for diastereoselective synthesis of substituted 1-(diethoxyphosphoryl) cyclopropanecarboxylates.

Experimental Section

General. Reagents were purchased from commercial sources and used as received without purification. Solvents were dried by standard procedures. Diols **1a**,¹⁰ **1b**¹¹ and **1c**¹² were obtained according to the literature procedures. NMR spectra were recorded on a Bruker DPX 250 instrument at 250.13 MHz for ¹H and 62.9 MHz for ¹³C and 101.3 MHz for ³¹P NMR, respectively, using tetramethylsilane as internal and 85% H₃PO₄ as external standard. The multiplicities of carbons were determined by DEPT experiments. IR spectra were measured on Specord M80 (Zeiss) instrument. Elemental analyses were performed on Perkin-Elmer PE 2400 analyzer. Melting points were determined in open capillaries and were uncorrected.

X-ray crystal structure analysis

A colourless single crystal of **5** (0.1 × 0.2 × 0.6 mm) was obtained by a slow evaporation from the chloroform-acetone mixture. X-ray data were collected on the Bruker Smart APEX diffractometer at room temperature with a graphite monochromatized MoK α radiation. Crystal structure was solved with direct methods and further refined using full matrix least squares technique. Crystal data and structure analysis parameters are summarized in Table 1. The following computer programs were applied during the analysis: data collection *SMART*,¹⁷ data reduction *SAINT-PLUS*,¹⁸ absorption correction *SADABS*,¹⁹ structure solution, refinement, and molecular graphics *SHELXTL*.²⁰

Crystallographic data (excluding structure factors) for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 764399. Copies of the data can be obtained free of charge on application

to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. Any request should be accompanied by a full literature citation.

Table 1. Crystal data and structural refinement details for **5**

Parameters	5
Empirical formula	C ₁₆ H ₂₃ O ₆ P
Formula weight	356.32
Temperature	293 (2) K
Wavelength	0.71073 Å
Crystal system, space group	monoclinic, <i>P</i> 2 ₁
Unit cell dimensions	<i>a</i> = 10.7927(9), <i>b</i> = 7.0051(5), <i>c</i> = 12.4943(10) Å, β = 113.107(3) °
<i>Z</i>	2
Unit cell volume	<i>V</i> = 868.83(12) Å ³
Density (calculated)	1.362 g cm ⁻³
Absorption coefficient	0.19 mm ⁻¹
<i>F</i> (000)	378.0
Crystal size	0.1 × 0.2 × 0.6 mm
Max. theta for the data collection	25.0°
Index ranges	-12 ≤ <i>h</i> ≤ 12, -8 ≤ <i>k</i> ≤ 8, -14 ≤ <i>l</i> ≤ 14
Number of collected reflections	20942
Number of independent reflections	3069 (<i>R</i> _{int} =0.023)
Absorption correction	multi-scan (Sadabs)
Refinement method	Full-matrix least –squares on <i>F</i> ²
Data/restraints/parameters	3069/0/258
Goodness of fit on <i>F</i> ²	1.071
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0542, <i>wR</i> ² = 0.1490
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0547, <i>wR</i> ² = 0.1504
Max. and min. on a difference Fourier map	0.474 and -0.302 eÅ ⁻³

General procedure for preparation 2,2-Dioxo-1,3,2-dioxathiolanes (2a-d)

(Dioxathiolanes **2a-d** were obtained by general procedure)¹

2,2-Dioxo-1,3,2-dioxathiolane-4-carboxylic acid ethyl ester (2a). Yield: (90%); yellowish oil.

¹H NMR (CDCl₃): δ 1.36 (t, ³*J* = 7.2 Hz, 3H, CH₃CH₂O); 4.37 (q, ³*J* = 7.2 Hz, 2H, CH₂O); 4.84 (dd, ²*J* = 9.0 Hz, ³*J* = 5.7 Hz, 1H, CHCHH); 4.92 (dd, ²*J* = 9.0 Hz, ³*J* = 7.2 Hz, 1H, CHCHH); 5.27 (dd, ³*J* = 7.2 Hz, ³*J* = 5.7 Hz, 1H, CHCH₂). ¹³C NMR (CDCl₃): δ 13.62 (s, CH₃CH₂O); 63.21 (s, CH₂O); 69.77 (s, CHCH₂); 75.80 (s, CHCH₂); 164.95 (s, C=O). IR (film) ν(C=O) 1752.

4-Diethoxymethyl-2,2-dioxo-1,3,2-dioxathiolane (2b). Yield: (70%); yellow oil. ¹H NMR (CDCl₃): δ 1.24 (t, ³*J* = 7.0 Hz, 3H, CH₃CH₂O); 1.26 (t, ³*J* = 7.0 Hz, 3H, CH₃CH₂O); 3.58 ÷ 3.82

(m, 5H, CH_2O , CH_2CHCH , CH_2CH); 3.98 ÷ 4.05 (m, 2H, CH_2O); 4.67 (d, $^3J = 5.0$ Hz, 1H, CH_2CHCH). ^{13}C NMR (MHz , CDCl_3): δ 14.82 (s, $\text{CH}_3\text{CH}_2\text{O}$); 14.86 (s, $\text{CH}_3\text{CH}_2\text{O}$); 64.22 (s, CH_2O); 65.18 (s, CH_2O); 68.17 (s, CH_2CHCH); 79.57 (s, CH_2CHCH); 99.92 (s, CH_2CHCH).

4-Benzylloxymethyl-2,2-dioxo-1,3,2-dioxathiolane (2c).² Yield: (85%); yellowish oil. ^1H NMR (CDCl_3): δ 3.78 (d, $^3J = 5.2$ Hz, 2H, CHCH_2OBn); 4.50 ÷ 4.76 (m, 4H, CH_2Ph , CHCH_2O); 4.99 ÷ 5.10 (m, 1H, CHO); 7.33 ÷ 7.41 (m, 5H, CH_{Ar}).

4-Butyl-2,2-dioxo-1,3,2-dioxathiolane (2d).¹³ Yield: (95%); yellowish oil. ^1H NMR (CDCl_3): δ 0.94 (t, $^3J = 6.5$ Hz, 3H, CH_3CH_2); 1.35 ÷ 1.54 (m, 4H, $(\text{CH}_2)_2$); 1.70 ÷ 1.81 (m, 1H, CH_2CHHCHO); 1.89 ÷ 2.02 (m, 1H, CH_2CHHCHO); 4.34 (dd, $^2J = 8.5$ Hz, $^3J = 8.2$ Hz, 1H, CHCHHO); 4.71 (dd, $^2J = 8.5$ Hz, $^3J = 6.0$ Hz, 1H, CHCHHO); 4.92 ÷ 5.03 (m, 1H, CHO).

General procedure for preparation 1-(diethoxyphosphoryl)cyclopropanecarboxylates 4a-d

To a stirred suspension of NaH (0.15g, 6.0mmol) in THF (25mL) triethylphosphonoacetate **3** (0.60mL, 3.0mmol) was added at room temperature. After stirring for 0.5h a solution of corresponding sulfate **2** (3.0mmol) in THF (10mL) was added and the resulting mixture was stirred at room temperature for 0.5h and then at reflux for 8h. After that time, the reaction mixture was poured into water (5mL), extracted with DCM (3x10mL) and organic layer was dried over MgSO_4 . Removal of the solvent gave the crude products **4**, which were purified by column chromatography (silica gel, eluent: chloroform/acetone 80:20).

trans-Diethyl 1-(diethoxyphosphoryl)cyclopropane-1,2-dicarboxylate (4a). Yield: 0.62 g (64%); colorless oil. $R_f = 0.30$. ^{31}P NMR (C_6D_6): δ 17.58. ^1H NMR (C_6D_6): δ 1.26 (t, $^3J_{\text{HH}} = 7.0$ Hz, 3H, $\text{CH}_3\text{CH}_2\text{O}$); 1.27 (t, $^3J_{\text{HH}} = 7.0$ Hz, 3H, $\text{CH}_3\text{CH}_2\text{O}$); 1.35 (td, $^3J_{\text{HH}} = 7.0$ Hz, $^4J_{\text{PH}} = 0.7$ Hz, 3H, $\text{CH}_3\text{CH}_2\text{OP}$); 1.37 (td, $^3J_{\text{HH}} = 7.0$ Hz, $^4J_{\text{PH}} = 0.7$ Hz, 3H, $\text{CH}_3\text{CH}_2\text{OP}$); 1.70 (ddd, $^3J_{\text{PH}} = 16.2$ Hz, $^3J_{\text{HH}} = 8.5$ Hz, $^2J_{\text{HH}} = 4.5$ Hz, 1H, PCCHH); 1.92 (ddd, $^3J_{\text{PH}} = 13.0$ Hz, $^3J_{\text{HH}} = 6.2$ Hz, $^2J_{\text{HH}} = 4.0$ Hz, 1H, PCCHH); 2.45 (ddd, $^3J_{\text{PH}} = 16.0$ Hz, $^3J_{\text{HH}} = 8.5$ Hz, $^3J_{\text{HH}} = 6.2$ Hz, 1H, PCCH); 4.10 ÷ 4.25 (m, 8H, $2\times\text{CH}_2\text{OP}$, $2\times\text{CH}_2\text{O}$). ^{13}C NMR (CDCl_3): δ 13.49 (s, $\text{CH}_3\text{CH}_2\text{O}$); 13.64 (s, $\text{CH}_3\text{CH}_2\text{O}$); 15.78 (d, $^3J_{\text{PC}} = 6.0$ Hz, $\text{CH}_3\text{CH}_2\text{OP}$); 15.83 (s, PCCH_2); 24.17 (s, PCCH); 28.70 (d, $^1J_{\text{PC}} = 177.95$ Hz, PC); 60.95 (s, CH_2O); 61.42 (s, CH_2O); 62.88 (s, CH_2OP); 62.90 (d, $^2J_{\text{PC}} = 5.60$ Hz, CH_2OP); 165.70 (d, $^2J_{\text{PC}} = 4.9$ Hz, C=O); 168.81 (d, $^3J_{\text{PC}} = 4.0$ Hz, C=O). IR (film) $\nu_{(\text{C=O})}$ 1740, $\nu_{(\text{P=O})}$ 1220, $\nu_{(\text{P-O})}$ 1024. Anal. Calcd. for $\text{C}_{13}\text{H}_{23}\text{O}_7\text{P}$: C 48.45, H 7.19. Found: C 48.36, H 7.21.

trans-Ethyl 2-(diethoxymethyl)-1-(diethoxyphosphoryl)cyclopropanecarboxylate (4b). Yield: 0.64 g (60%); colorless oil. $R_f = 0.32$. ^{31}P NMR (C_6D_6): δ 23.08. ^1H NMR (C_6D_6): δ 1.22 ÷ 1.33 (m, 6H, $2\times\text{CH}_3\text{CH}_2\text{O}$); 1.34 (t, $^3J_{\text{HH}} = 7.0$ Hz, 6H, $2\times\text{CH}_3\text{CH}_2\text{OP}$); 1.43 (t, $^3J_{\text{HH}} = 7.0$ Hz, 3H, $\text{CH}_3\text{CH}_2\text{O}$); 1.80 ÷ 1.90 (m, 3H, PCCH_2 , PCCH); 3.67 ÷ 3.84 (m, 4H, $2\times\text{CH}_2\text{O}$); 4.00 ÷ 4.25 (m, 4H, $2\times\text{CH}_2\text{OP}$); 4.34 (q, $^3J_{\text{HH}} = 7.0$ Hz, 2H, CH_2O); 4.68 (d, $^3J_{\text{HH}} = 7.0$ Hz, OCHO). ^{13}C NMR (CDCl_3): δ 13.72 (s, $\text{CH}_3\text{CH}_2\text{O}$); 14.77 (s, $\text{CH}_3\text{CH}_2\text{O}$); 14.80 (s, $\text{CH}_3\text{CH}_2\text{O}$); 15.91 (s, $\text{CH}_3\text{CH}_2\text{OP}$); 15.99 (s, $\text{CH}_3\text{CH}_2\text{OP}$); 20.26 (d, $^2J_{\text{PC}} = 4.9$ Hz, PCCH); 21.71 (d, $^1J_{\text{PC}} = 178.4$ Hz, PC); 27.38 (s, PCCH_2); 61.35 (s, CH_2O); 62.22 (2d, $^2J_{\text{PC}} = 5.8$ Hz, CH_2OP); 63.56 (s, CH_2O);

64.89 (s, CH₂O); 79.34 (s, OCHO); 168.73 (d, ²J_{PC} = 4.5 Hz, C=O). IR (film) ν(C=O) 1748, ν(P=O) 1264, ν(P-O) 1024. Anal. Calcd. for C₁₅H₂₉O₇P: C 51.13, H 8.30. Found: C 51.26, H 8.34.

trans-Ethyl 2-(benzyloxymethyl)-1-(diethoxyphosphoryl)cyclopropanecarboxylate (4c). Yield: 0.70 g (63%); colorless oil. R_f = 0.38. ³¹P NMR (C₆D₆): δ 23.14. ¹H NMR (C₆D₆): δ 1.23 (t, ³J_{HH} = 7.2 Hz, 3H, CH₃CH₂O); 1.31 (t, ³J_{HH} = 7.0 Hz, 6H, 2xCH₃CH₂OP); 1.54 ÷ 1.68 (m, 2H, PCCH₂); 2.12 ÷ 2.27 (m, 1H, PCCH); 3.48 (dd, ²J_{HH} = 10.5 Hz, ³J_{HH} = 8.7 Hz, 1H, CHHOCH₂Ph); 3.78 (dd, ²J_{HH} = 10.5 Hz, ³J_{HH} = 5.5 Hz, 1H, CHHOCH₂Ph); 4.11 ÷ 4.23 (m, 6H, 2xCH₂OP, CH₂O); 4.40 (s, 2H, OCH₂Ph); 7.27 ÷ 7.35 (m, 5H, CH_{Ar}). ¹³C NMR (CDCl₃): δ 13.87 (s, CH₃CH₂O); 16.10 (d, ³J_{PC} = 6.7 Hz, CH₃CH₂OP); 16.20 (d, ³J_{PC} = 6.1 Hz, CH₃CH₂OP); 16.58 (s, PCCH₂); 23.77 (d, ¹J_{PC} = 188.5 Hz, PC); 26.31 (d, ²J_{PC} = 2.8 Hz, PCCH); 61.43 (s, CH₂O); 62.47 (d, ²J_{PC} = 6.2 Hz, CH₂OP); 62.57 (d, ²J_{PC} = 6.5 Hz, CH₂OP); 67.40 (s, CHCH₂O); 72.42 (s, OCH₂Ph); 127.20 (s, 2xCH_{Ar}); 127.37 (s, CH_{Ar}); 128.10 (s, 2xCH_{Ar}); 136.40 (s, C_{Ar}); 166.27 (s, C=O). IR (film) ν(C=O) 1724, ν(P=O) 1270, ν(P-O) 1028. Anal. Calcd. for C₁₈H₂₇O₆P: C 58.37, H 7.35. Found: C, 58.49; H, 7.31.

trans-Ethyl 2-(butyl)-1-(diethoxyphosphoryl)cyclopropanecarboxylate (4d). Yield: 0.58 g (63%); colorless oil. R_f = 0.48. ³¹P NMR (C₆D₆): δ 24.30. ¹H NMR (C₆D₆): δ 0.89 (t, ³J_{HH} = 7.0 Hz, 3H, CH₃CH₂); 1.29 (t, ³J_{HH} = 7.2 Hz, 3H, CH₃CH₂O); 1.34 (t, ³J_{HH} = 7.0 Hz, 3H, CH₃CH₂OP); 1.35 (t, ³J_{HH} = 7.0 Hz, 3H, CH₃CH₂OP); 1.23 ÷ 1.60 (m, 9H, (CH₂)₃, PCCH₂, PCCH); 4.14 (dq, ³J_{PH} = 7.0 Hz, ³J_{HH} = 7.0 Hz, 2H, CH₂OP); 4.15 (dq, ³J_{PH} = 7.0 Hz, ³J_{HH} = 7.0 Hz, 2H, CH₂OP); 4.16 (q, ³J_{HH} = 7.2 Hz, 1H, CHHO); 4.21 (q, ³J_{HH} = 7.2 Hz, 1H, CHHO). ¹³C NMR (CDCl₃): δ 13.62 (s, CH₃CH₂); 13.90 (s, CH₃CH₂O); 16.09 (d, ³J_{PC} = 6.1 Hz, CH₃CH₂O)P); 18.17 (d, ²J_{PC} = 2.8 Hz, PCCH₂); 21.93 (s, CH₃CH₂); 24.96 (d, ¹J_{PC} = 189.5 Hz, PC); 26.96 (s, CH₃CH₂CH₂); 27.03 (s, PCCH); 30.87 (s, CH₂CH₂CH); 61.05 (s, CH₂O); 62.08 (d, ²J_{PC} = 6.2 Hz, CH₂OP); 62.18 (d, ²J_{PC} = 6.3 Hz, CH₂OP); 168.04 (d, ²J_{PC} = 7.2 Hz, C=O). IR (film) ν(C=O) 1724, ν(P=O) 1252, ν(P-O) 1028. Anal. Calcd. for C₁₄H₂₇O₅P: C 54.89, H 8.88. Found C 55.00, H 8.84.

Procedure for preparation *trans*-2-Benzoyloxymethyl-1-(diethoxyphosphoryl)cyclopropanecarboxylic acid (5)

To a solution of cyclopropanecarboxylate **4c** (0.37 g, 1.00 mmol) in ethyl alcohol (5 mL) a solution of NaOH (0.08 g ; 2.00 mmol) in water (0.5 mL) was added and the reaction mixture was stirred at room temperature for 2 days. Then the solvent was evaporated and residue was dissolved in water (10 mL) and extracted with diethyl ether (3x10 mL). Then the water layer was acidified to pH 1 with 3N HCl and extracted with dichloromethane (3x10 mL). The combined organic layers were dried (MgSO₄) and evaporated under reduced pressure. The residue crystallized on standby to give acid **5** as white solid, which was collected by filtration from diethyl ether.

trans-2-(Benzoyloxymethyl)-1-(diethoxyphosphoryl)cyclopropanecarboxylic acid (5). Yield: 0.33 g (97%); white crystal; m.p. = 102-104 °C. ³¹P NMR (CDCl₃): δ 27.42. ¹H NMR (CDCl₃): δ 1.30 (td, ³J_{HH} = 7.0 Hz, ⁴J_{PH} = 0.7 Hz, 6H, 2xCH₃CH₂OP); 1.61 (dd, ³J_{PH} = 12.2 Hz, ³J_{HH} = 8.5

Hz, 2H, PCCH₂); 2.23 (dddd, $^3J_{\text{PH}} = 16.5$ Hz, $^3J_{\text{HH}} = 10.0$ Hz, $^3J_{\text{HH}} = 8.5$ Hz, $^3J_{\text{HH}} = 8.5$ Hz, $^3J_{\text{HH}} = 5.7$ Hz 1H, PCCH); 3.55 (dd, $^2J_{\text{HH}} = 10.7$ Hz, $^3J_{\text{HH}} = 8.5$ Hz, 1H, CHHOCH₂Ph); 3.78 (dd, $^2J_{\text{HH}} = 10.7$ Hz, $^3J_{\text{HH}} = 5.7$ Hz, 1H, CHHOCH₂Ph); 4.16 (dq, $^3J_{\text{PH}} = ^3J_{\text{HH}} = 7.0$ Hz, 1H, CHHOP); 4.17 (dq, $^3J_{\text{PH}} = ^3J_{\text{HH}} = 7.0$ Hz, 1H, CHHOP); 4.18 (dq, $^3J_{\text{PH}} = ^3J_{\text{HH}} = 7.00$ Hz, 2H, CH₂OP); 4.47 (s, 2H, OCH₂Ph); 7.25 ÷ 7.32 (m, 5H, CH_{Ar}). ¹³C NMR (CDCl₃): δ 16.04 (d, $^3J_{\text{PC}} = 6.1$ Hz, CH₃CH₂OP); 16.13 (d, $^3J_{\text{PC}} = 5.0$ Hz, CH₃CH₂OP); 17.24 (s, PCCH₂); 23.38 (d, $^1J_{\text{PC}} = 190.9$ Hz, PC); 26.95 (s, PCCH); 63.01 (d, $^2J_{\text{PC}} = 6.5$ Hz, CH₂OP); 63.11 (d, $^2J_{\text{PC}} = 6.5$ Hz, CH₂OP); 67.22 (s, CH₂OCH₂Ph); 72.43 (s, OCH₂Ph); 127.36 (s, 2×CH_{Ar}); 128.13 (s, CH_{Ar}); 128.14 (s, 2×CH_{Ar}); 137.94 (s, C_{Ar}); 170.34 (d, $^2J_{\text{PC}} = 8.5$ Hz, C=O). IR (film) $\nu_{\text{(C=O)}}$ 1764, $\nu_{\text{(P=O)}}$ 1264, $\nu_{\text{(P-O)}}$ 1020. Anal. Calcd. for C₁₆H₂₃O₆P: C 56.14, H 6.77. Found C, 56.23; H, 6.80.

Acknowledgements

The authors thank Professor Ryszard Bodalski (Technical University of Lodz) for stimulating discussions.

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