Pergamon

Tetrahedron Letters 42 (2001) 4365–4368

TETRAHEDRON LETTERS

# Addition of secondary amines to alkynylphosphonates

Anna E. Panarina, Alla V. Dogadina, Valentin I. Zakharov and Boris I. Ionin*

*Laboratory of Organophosphorus Chemistry, Organic Chemistry Department, St. Petersburg State Technological Institute (Technical University), 26 Moskovskii Prospect, St. Petersburg 198013, Russia*

Received 29 November 2000; revised 10 April 2001; accepted 27 April 2001

**Abstract**—Addition of secondary amines to alkynylphosphonates catalyzed by Cu(I) salts proceeds regio- and stereospecifically to form (*E*)-2-(dialkylamino)alkenylphosphonates. The *E*-configuration was proved by analysis of $^{13}C$–$^{31}P$ vicinal spin–spin coupling constants in the NMR spectra of the products and authentic model compounds. The $^{3}J_{PC}$ constants in the model compounds fall in the range of 6–12 Hz for the *cis* arrangement of the coupled nuclei and are equal to or higher than 16 Hz for the *trans* configuration. Related coupling constants in the addition products are around 5 Hz, that is, corresponding to *cis* coupling. 

2-Dialkylaminoalkenylphosphonates can be regarded as precursors of β-aldo- and β-ketophosphonates.[1] They are also interesting as models of push–pull alkenes for both chemical and biochemical investigations.[2] Recently, a synthetic route to such compounds was developed by Kazankova, Beletskaya and co-workers[3] who prepared diethyl 2-phenyl-2-piperidylethenephosphonate by cross-coupling of the corresponding 2-bromo-1-piperidylstyrene with triethyl phosphite in the presence of $NiBr_2$ in 55% yield. Herein, we report on a convenient route to 2-dialkylaminoalkenylphosphonates based on the addition of amines to the triple bond of acetylenic phosphonates.

In 1963 Saunders and Simpson prepared (*E*)-2-diethylaminoethenephosphonate by reaction of diethylamine with ethynylphosphonate. The reaction is exothermic and results in a high yield of the product.[4] More recently, Acheson and co-workers noted[5] that ethynylphosphonate reacts with secondary amines to form mixtures of *E* and *Z* isomers. Propynylphosphonate adds secondary amines to form 2-dialkylamino-1-propenylphosphonates in poor yield (10–15%) contaminated with 2,2-bis(dialkylamino)propanylphosphonate.[6] Addition of primary and secondary amines to ethynyldiphenylphosphine oxide in the presence of butyllithium was studied in detail, and was

**Table 1.** β-Enaminophosphonates **3** (*E*)-$(EtO)_2P(O)CH{=}C(NR^2_2)R^1$[a]

| No. | $R^1$ | $NR^2_2$ | | Reaction conditions | Method | Time (h) | Yield (%)[b] | Bp (mmHg) |
|---|---|---|---|---|---|---|---|---|
| 1 | H | $NEt_2$ | **3a** | EtOH | A | 0.5 | 42 | 109 (0.1)[c] |
| 2 | H | $N(CH_2)_5$ | **3b** | MeOH | B | 12 | 36 | 112 (0.1) |
| 3 | H | $N(CH_2)_4O$ | **3c** | MeOH | B | 18 | 80 | 163 (0.5) |
| 4 | $CH_3$ | $NEt_2$ | **3d** | EtOH, Cu(I)Cl | A | 2.5 | 38 | 126 (0.1) |
| 5 | $CH_3$ | $N(CH_2)_5$ | **3e** | MeOH, Cu(I)Cl | B | 22 | 41 | 170 (0.5) |
| 6 | $CH_3$ | $N(CH_2)_4O$ | **3f** | MeOH, Cu(I)Cl | B | 26 | 45 | 180 (0.5) |
| 7 | $C_2H_5$ | $NEt_2$ | **3g** | $Et_2O$, Cu(I)Cl | A | 9.3 | 36 | 130 (0.1) |
| 8 | $C_2H_5$ | $N(CH_2)_5$ | **3h** | MeOH, Cu(I)Cl | B | 26.5 | 35 | 156 (0.25) |
| 9 | $C_6H_5$ | $NEt_2$ | **3i** | EtOH, Cu(I)Cl | A | 3.5 | 41 | 156 (0.1) |
| 10 | $C_6H_5$ | $N(CH_2)_5$ | **3j** | MeOH, Cu(I)Cl | B | 50 | 40 | 160 (0.1) |
| 11 | $C_6H_5$ | $N(CH_2)_4O$ | **3k** | MeOH, Cu(I)Cl | B | 57 | 38 | 165 (0.1) |

[a] All products gave satisfactory $^1H$, $^{31}P$, $^{13}C$ NMR and IR spectra.
[b] All products were initially formed quantitatively, but partially hydrolyzed into the ketone and decomposed during the isolation process.
[c] $^{13}C$ and $^{31}P$ NMR and IR spectra of the product agree with the published data.[5]

* Corresponding author. E-mail: bi@thesa.ru

0040-4039/01/$ - see front matter 
PII: S0040-4039(01)00711-0

shown to lead to the corresponding (*E*)-2-aminovinyldiphenylphosphine oxides.[7] Non-catalyzed addition of primary amines to other alkynyldiphenylphosphine oxides results in the formation of mixtures of *E* and *Z* isomers.[8]

We found that addition of secondary amines to alkynylphosphonates proceeds much better in the presence of a Cu(I) salt. Rousselet and co-workers noted earlier[9] that addition of primary and secondary amines to nitriles in the presence of Cu(I) salts proceeds to give high yields (80–100%) of the addition compounds.

With diethyl ethynylphosphonate, addition of secondary amines both in the presence and absence of Cu(I) salts proceeds as a *cis*-addition and leads to *E* isomers of the corresponding 2-dialkylaminoethenephosphonates, in agreement with the data published by Acheson and co-workers.[5] With less reactive substituted ethynylphosphonates **1**, the reaction in the absence of Cu(I) catalyst does not occur at a noticeable rate even on heating the reactants in an ampoule to 120°C. A catalytic amount of Cu(I) salt allows the addition to proceed regio- and stereospecifically, affording (*E*)-2-(dialkylamino)-ethenylphosphonates (Table 1). The reaction was carried out in a polar solvent, such as EtOH, MeOH, or $Et_2O$, which have been noted to increase the reaction rate in the cases alkynylphosphine oxides[8] and nitriles.[9]

Establishing the geometric configuration of the 2-dialkylaminoalkenephosphonates **3** is difficult and was not ascertained earlier.[3,10] For elucidation of the configuration of enaminophosphonates **3**, we used the well-known steric dependence of the vicinal spin–spin coupling constant. The angular dependence of $^3J$ coupling was first established for H–H pairs[11] and confirmed, in part, by our investigations for $^1H$–$^{31}P$[12] and $^{31}P$–$^{31}P$[13] couplings. However, steric variations of $^3J$ coupling for the $^{31}P$–$^{13}C$ pair, which could be useful in our case, has scarcely been studied.[14,15]

Therefore, we performed the synthesis and study of the $^{13}C$ NMR spectra of several model compounds with rigorously defined structures.

A comparison of the NMR parameters of the β-enaminophosphonates obtained and certain model compounds (Table 2), together with the use of the well-known appearance of $^3J$ constants in alkenes, which is normally greater in *trans* derivatives,[16] allowed the unambiguous assignment of the *E* configuration (*cis* addition of amine) for the compounds **3**.

Additionally, we proved the structures by $^1H$ NMR experiments with lanthanide shift reagents. For the β-enaminophosphonates obtained from propynylphosphonate we succeeded in identifying the allylic spin–spin

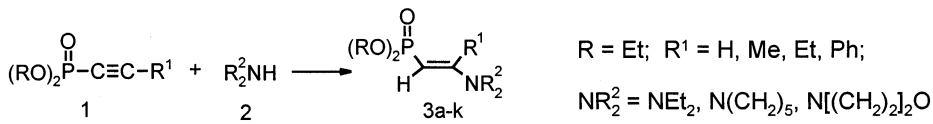


**Table 2.** Parameters of $^{13}C$ NMR spectra of model compounds and β-enaminophosphonates **3** $(C_2H_5O)_2P(O)CH{=}C(X)R^1$

| No. | $R^1$ | X | Isomer | Chemical shifts (ppm) $(C_2H_5O)_2P(O)C^1H{=}C^2(X)(R^1)^3$ | | | Spin–spin coupling constants (Hz) | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | $\delta_1$ | $\delta_2$ | $\delta_3$ | $^1J_{PC}$ | $^2J_{PC}$ | $^3J_{PC}$ |
| 1 | Me | Me | – | 111.71 | 158.36 | 20.17 (*Z*)<br>27.25 (*E*) | 189.48 | 10.7 | 6.54 (*Z*)<br>24.21 (*E*) |
| 2 | Me | H | *E* | 116.34 | 148.85 | 19.43 | 188.58 | 4.97 | 23.77 |
| 3 | Me | H | *Z* | 116.80 | 148.62 | 15.56 | 188.68 | 5.00 | 10.37 |
| 4[a] | Me | Cl | *Z* | 122.32 | 154.80 | 29.9 | 175.32 | 6.04 | 19.3 |
| 5 | Ph | H | *E* | 113.46 | 147.73 | 134.50 | 191.55 | 6.7 | 23.67 |
| 6 | Ph | H | *Z* | 115.54 | 147.29 | 134.28 | 184.16 | 5.86 | 7.0 |
| 7 | Ph | Cl | *Z* | 112.67 | 149.57 | 136.62 | 199.05 | 3.17 | 16.4 |
| 8 | *t*-Bu | H | *Z* | 113.26 | 161.22 | 33.33 | 186.21 | 4.73 | 6.24 |
| 9 | *t*-Bu | H | *E* | 110.97 | 161.92 | 33.69 | 188.01 | 3.52 | 20.08 |
| 10 | *t*-Bu | Cl | *Z* | 111.51 | 163.24 | 40.66 | 196.88 | 2.5 | 12.53 |
| 11[a] | *t*-Bu | Cl | *Z* | 119.36 | 167.38 | 41.30 | 160.54 | 7.54 | 14.90 |
| **3b** | H | $N(CH_2)_5$ | *E* | 72.44 | 153.48 | – | 209.2 | 20.1 | – |
| **3c** | H | $N[(CH_2)_2]O$ | *E* | 75.50 | 153.62 | – | 201.31 | 19.32 | – |
| **3d** | Me | $NEt_2$ | *E* | 72.97 | 158.75 | 17.15 | 217.34 | 21.0 | 5.0 |
| **3e** | Me | $N(CH_2)_5$ | *E* | 76.02 | 160.06 | 17.42 | 212.7 | 19.33 | 3.57 |
| **3f** | Me | $N[(CH_2)_2]O$ | *E* | 79.19 | 160.64 | 16.95 | 212.9 | 19.17 | 2.82 |
| **3g** | Et | $NEt_2$ | *E* | 72.54 | 164.43 | 22.33 | 217.33 | 21.6 | 5.1 |
| **3h** | Et | $N(CH_2)_5$ | *E* | 75.63 | 165.99 | 23.46 | 215.7 | 21.72 | 5.18 |
| **3i** | Ph | $NEt_2$ | *E* | 76.60 | 161.18 | 135.2 | 217.82 | 17.1 | 5.6 |
| **3j** | Ph | $N(CH_2)_5$ | *E* | 81.19 | 164.05 | 136.45 | 214.4 | 17.36 | 4.07 |
| **3k** | Ph | $N[(CH_2)_2]O$ | *E* | 83.93 | 163.77 | 135.24 | 212.6 | 16.31 | 4.07 |

[a] Phosphonic dichloride.

coupling constant $^4J_{HP}$, which was found to be equal to 1.5 Hz. This value corresponds to the *cisoid* allylic coupling, while the corresponding *transoid* constant has been determined in the range 0–0.5 Hz.[12]

We also found that the required β-(dialkylamino)alkenylphosphonates can also be prepared from the corresponding β-chloroalkenylphosphonates **4**, the same *E* isomers being obtained. However, the chloroalkenylphosphonates initially eliminate hydrogen chloride to form acetylenic compounds **1**, which add amine **2** in the second step. Formation of acetylenes was monitored by $^1$H NMR spectroscopy.

$$(RO)_2\underset{\mathbf{4}}{P(O)CH{=}CClR^1} + \underset{\mathbf{2}}{R^2{}_2NH} \rightarrow [\underset{\mathbf{1}}{(RO)_2P(O)C{\equiv}CR^1}] \rightarrow (E)\text{-}\underset{\mathbf{3d,i}}{(RO)_2P(O)CH{=}C(NR^2{}_2)R^1}$$

$R^1 = Me$; $R^2 = Et$

The β-(dialkylamino)alkenylphosphonates obtained are easily hydrolyzed with water to form β-ketophosphonates **5**. The latter are interesting as reagents for Horner–Emmons synthesis[1] and also are known as effective metal extractors.[17]

$$\underset{\mathbf{3a\text{-}k}}{(RO)_2P(O)CH{=}C(NR^2{}_2)R^1} + H_2O \rightarrow \underset{\mathbf{5a\text{-}k}}{(RO)_2P(O)CH{-}C(=O)R^1}$$

## Experimental

**General procedure for the preparation of 2-(dialkylamino)alkenylphosphonates 3. Method A**. A 20 ml flask equipped with a reflux condenser and magnetic stirrer was purged with dry argon and the corresponding solvent (10 ml), alkynylphosphonate **1** (8.5 mmol) and amine (9.4 mmol) were added, and in some cases Cu(I)Cl 50 mg was added as a catalyst. The reaction mixture was stirred under reflux for several hours and monitored by $^1$H NMR spectroscopy. After completion of the reaction, the mixture was filtered to separate the catalyst, the solvent was removed in vacuo and the residue was distilled in a vacuum at 0.1 mmHg. **Method B**. Alkynylphosphonate (8.5 mmol) and amine (9.4 mmol) were sealed in an ampoule with 2 ml of methanol and, in some experiments, with 50 mg of Cu(I)Cl catalyst. The mixture was heated on a bath for several hours at 100–110°C. Then the product was isolated by distillation in a vacuum (see Table 1).

**(*E*)-Diethyl-2-piperidinoeth-1-enylphosphonate (3b)**: mp 112°C (0.1 mmHg); $^1$H NMR (200 MHz): 1.28 (t, 6H, $CH_3$), 1.54 (m, 6H, $CH_2$ piper.), 3.11 (t, 4H, $CH_2$-N), 3.97 (q, 4H, $CH_2$-O), 4.14 (d, 1H, $^2J_{HP}$ = 6 Hz, CH), 6.93 (t, 1H, $^3J_{HH}$ = 14.5 Hz, $^3J_{HP}$ = 15.25 Hz, CH); $^{13}$C NMR (50 MHz): 15.92 ($CH_3$), 23.83 (*p*-$CH_2$, piper.), 24.27 (*m*-$CH_2$, piper), 48.75 ($CH_2$-N), 60.33 ($CH_2$-O), 72.44 (d, $^1J_{PC}$ = 209.2 Hz, CH), 153.44 (d, $^2J_{PC}$ = 20.1 Hz, =C–N); $^{31}$P NMR (80 MHz): 29.45.

**(*E*)-Diethyl-2-morpholinoeth-1-enylphosphonate (3c)**: mp 163°C (0.5 mmHg); $^1$H NMR (200 MHz): 1.53 (t, 6H, $CH_3$), 3.08 (t, 4H, $CH_2$-N), 3.61 (t, 4H, $CH_2$-O), 3.94 (q, 4H, $CH_2$-O), 4.18 (d, 1H, $^2J_{HP}$ = 12 Hz, CH), 6.9 (t, 1H, $^3J_{HH}$ = 14.8 Hz, $^3J_{HP}$ = 14.8 Hz, CH); $^{13}$C NMR (50 MHz): 16.27 ($CH_3$), 42.9 ($CH_2$-N), 60.88 ($CH_2$-O), 65.97 ($CH_2$-O, morph.), 75.5 (d, $^1J_{PC}$ = 201.31 Hz, CH), 153.62 (d, $^2J_{PC}$ = 19.32 Hz, =C–N); $^{31}$P NMR (80 MHz): 27.59; IR (KBr): 2970, 1600, 1200, 1020 cm$^{-1}$.

**(*E*)-Diethyl-2-*N*-diethylaminoprop-1-enylphosphonate (3d)**: mp 126°C (0.1 mmHg); $^1$H NMR (200 MHz): 0.84 (t, 6H, $CH_3$), 1.01 (t, 6H, $CH_3$), 1.92 (d, 3H, $^4J_{HP}$ = 1.6 Hz, $CH_3$), 2.95 (q, 4H, $CH_2$-N), 3.46 (d, 1H, $^2J_{HP}$ = 9.81 Hz, CH), 3.71 (q, 4H, $CH_2$-O); $^{13}$C NMR (50 MHz): 12.66 ($CH_3$), 16.31 ($CH_3$), 17.15 (d, $^3J_{PC}$ = 5.0 Hz, $CH_3$), 43.79 ($CH_2$-N), 60.45 ($CH_2$-O), 72.97 (d, $^1J_{PC}$ = 217.34 Hz, CH), 158.75 (d, $^2J_{PC}$ = 21.0 Hz, =C–N); $^{31}$P NMR (80 MHz): 27.46; IR (KBr): 2970, 1558, 1213, 1029 cm$^{-1}$.

**(*E*)-Diethyl-2-piperidinoprop-1-enylphosphonate (3e)**: mp 170°C (0.5 mmHg); $^1$H NMR (200 MHz): 1.1 (t, 6H, $CH_3$), 1.38 (m, 6H, $CH_2$ piper.), 1.98 (d, 3H, $^4J_{HP}$ = 1.0 Hz, $CH_3$), 3.02 (t, 4H, $CH_2$-N), 3.87 (d, 1H, $^2J_{HP}$ = 9.75 Hz, CH), 3.88 (q, 4H, $CH_2$-O); $^{13}$C NMR (50 MHz): 15.8 ($CH_3$), 17.42 (d, $^3J_{PC}$ = 3.57 Hz, $CH_3$), 23.65 (*p*-$CH_2$, piper.), 24.7 (*m*-$CH_2$, piper), 46.69 ($CH_2$-N), 60.11 ($CH_2$-O), 76.02 (d, $^1J_{PC}$ = 212.7 Hz, CH), 160.06 (d, $^2J_{PC}$ = 19.33 Hz, =C–N); $^{31}$P NMR (80 MHz): 27.85; IR (KBr): 2970, 1560, 1220, 1029 cm$^{-1}$.

**(*E*)-Diethyl-2-morpholinoprop-1-enylphosphonate (3f)**: mp 180°C (0.5 mmHg); $^1$H NMR (200 MHz): 1.12 (t, 6H, $CH_3$), 2.02 (d, 3H, $^4J_{HP}$ = 2.0 Hz, $CH_3$), 2.98 (t, 4H, $CH_2$-N), 3.53 (t, 4H, $CH_2$-O), 3.8 (d, 1H, $^2J_{HP}$ = 9.0 Hz, CH), 3.85 (q, 4H, $CH_2$-O); $^{13}$C NMR (50 MHz): 15.8 ($CH_3$), 16.95 (d, $^3J_{PC}$ = 2.82 Hz, $CH_3$), 45.7 ($CH_2$-N), 60.29 ($CH_2$-O), 65.71 ($CH_2$-O, morph.), 79.19 (d, $^1J_{PC}$ = 212.9 Hz, CH), 160.64 (d, $^2J_{PC}$ = 19.17 Hz, =C–N); $^{31}$P NMR (80 MHz): 26.04; IR (KBr): 2970, 1560, 1213, 1024 cm$^{-1}$.

**(*E*)-Diethyl-2-*N*-diethylaminobut-1-enylphosphonate (3g)**: mp 130°C (0.1 mmHg); $^1$H NMR (200 MHz): 0.90 (t, 6H, $CH_3$), 0.93 (t, 3H, $CH_3$), 1.07 (t, 6H, $CH_3$), 2.4 (q, 2H, $CH_2$), 3.0 (q, 4H, $CH_2$-N), 3.48 (d, 1H, $^2J_{HP}$ = 9.8 Hz, CH), 3.79 (q, 4H, $CH_2$-O); $^{13}$C NMR (50 MHz): 12.91 ($CH_3$), 13.96 ($CH_3$, Et), 16.37 ($CH_3$), 22.33 (d, $^3J_{PC}$ = 5.1 Hz, $CH_2$, Et), 43.3 ($CH_2$-N), 60.45 ($CH_2$-O), 72.54 (d, $^1J_{PC}$ = 217.33 Hz, CH), 164.43 (d, $^2J_{PC}$ = 21.6 Hz, =C–N); $^{31}$P NMR (80 MHz): 27.17; IR (KBr): 2970, 1546, 1213, 1029 cm$^{-1}$.

**(*E*)-Diethyl-2-piperidinobut-1-enylphosphonate (3h)**: mp 156°C (0.25 mmHg); $^1$H NMR (200 MHz): 1.21 (t, 6H, $CH_3$), 1.25 (t, 3H, $CH_3$), 1.5 (m, 6H, $CH_2$ piper.), 2.57 (q, 2H, $CH_2$, Et), 3.08 (m, 4H, $CH_2$-N), 3.85 (d, 1H,

$^2J_{HP}$ = 10.3 Hz, CH), 3.93 (q, 4H, $CH_2$-O); $^{13}$C NMR (50 MHz): 13.02 ($CH_3$), 16.77 ($CH_3$), 23.46 (d, $^3J_{PC}$ = 5.18 Hz, $CH_3$), 25.14 ($CH_2$, piper), 47.07 ($CH_2$-N), 60.39 ($CH_2$-O), 75.63 (d, $^1J_{PC}$ = 215.7 Hz, CH), 165.99 (d, $^2J_{PC}$ = 21.72 Hz, =C–N); $^{31}$P NMR (80 MHz): 27.25; IR (KBr): 2973, 1629, 1233, 1013 cm$^{-1}$.

**(*E*)-Diethyl-2-*N*-diethylaminophenyleth-1-enylphosphonate (3i)**: mp 156°C (0.1 mmHg); $^1$H NMR (200 MHz): 0.75 (m, 12H, $CH_3$), 2.28 (q, 4H, $CH_2$-N), 3.42 (q, 4H, $CH_2$-O), 3.87 (d, 1H, $^2J_{HP}$ = 10.3 Hz, CH), 7.0 (m, 5H, arom.); $^{13}$C NMR (50 MHz): 11.7 ($CH_3$), 15.16 ($CH_3$), 42.71 ($CH_2$-N), 59.3 ($CH_2$-O), 76.6 (d, $^1J_{PC}$ = 217.82 Hz, CH), 126.65–127.54 (m, *p*-CH-arom.), 128.15 (*o*-CH-arom.), 135.2 (d, $^3J_{PC}$ = 5.6 Hz, C-*ipso*, arom.), 161.18 (d, $^2J_{PC}$ = 17.1 Hz, =C–N); $^{31}$P NMR (80 MHz): 24.14; IR (KBr): 2970, 1533, 1200, 1029 cm$^{-1}$. MS (EI) 310; *m*/*z* (%): 29 (77.9), 72 (51.7), 103 (51.3), 131 (34.4), 174 (100), 282 (29.3), 310 (60.7).

**(*E*)-Diethyl-2-piperidinophenyleth-1-enylphosphonate (3j)**: mp 160°C (0.1 mmHg); $^1$H NMR (200 MHz): 1.06 (t, 6H, $CH_3$), 1.55 (m, 6H, $CH_2$ piper.), 3.0 (m, 4H, $CH_2$-N), 4.11 (q, 4H, $CH_2$-O), 4.36 (d, 1H, $^2J_{HP}$ = 9.8 Hz, CH), 7.35 (m, 5H, arom.); $^{13}$C NMR (50 MHz): 15.82 (*m*-$CH_2$, piper.), 15.85 ($CH_3$), 25.23 (*p*-$CH_2$, piper.), 48.62 (*o*-$CH_2$, piper.), 60.34 ($CH_2$-O), 81.19 (d, $^1J_{PC}$ = 214.4 Hz, CH), 127.63 (*m*-CH-arom.), 128.33 (*p*-CH-arom.), 128.99 (*o*-CH-arom.), 136.45 (d, $^3J_{PC}$ = 4.07 Hz, C-*ipso*, arom.), 164.05 (d, $^2J_{PC}$ = 17.36 Hz, =C–N); $^{31}$P NMR (80 MHz): 24.6; IR (KBr): 2970, 1540, 1220, 1029 cm$^{-1}$.

**(*E*)-Diethyl-2-morpholinophenyleth-1-enylphosphonate (3k)**: mp 165°C (0.1 mmHg); $^1$H NMR (200 MHz): 0.97 (t, 6H, $CH_3$), 2.87 (t, 4H, $CH_2$-N), 3.55 (t, 4H, $CH_2$-O, morph.), 3.67 (q, 4H, $CH_2$-O), 4.37 (d, 1H, $^2J_{HP}$ = 9.2 Hz, CH), 7.27 (m, 5H, arom.); $^{13}$C NMR (50 MHz): 15.67 ($CH_3$), 47.59 ($CH_2$-N), 60.38 ($CH_2$-O), 65.94 ($CH_2$-O, morph.), 83.93 (d, $^1J_{PC}$ = 212.6 Hz, CH), 127.57 (*m*-CH-arom.), 128.75 (*p*-CH-arom.), 128.89 (*o*-CH-arom.), 135.24 (d, $^3J_{PC}$ = 4.07 Hz, C-*ipso*, arom.), 163.77 (d, $^2J_{PC}$ = 16.31 Hz, =C–N); $^{31}$P NMR (80 MHz): 23.12; IR (KBr): 2970, 1540, 1220, 1020 cm$^{-1}$.

## References


1. Walker, B. J. *Organophosphorus Reagents in Organic Synthesis*; Academic Press: London, 1979; pp. 155–206.
2. Lee, S.-L.; Hepburn, T. W.; Swartz, M. H.; Ammon, H. L.; Mariano, P. S.; Dunaway-Mariano, D. *J. Am. Chem. Soc.* **1992**, *114*, 7346–7354.
3. Kazankova, M. A.; Trostyanskaya, I. G.; Lutsenko, S. V.; Efremova, I. V.; Beletskaya, I. P. *Zh. Obshch. Khim.* **1999**, *35*, 452–458.
4. Saunders, B. C.; Simpson, P. *J. Chem. Soc.* **1963**, 3351–3357.
5. Acheson, R. M.; Ansel, P. J.; Murray, J. R. *J. Chem. Res. (S)* **1986**, 378–379.
6. Pudovik, A. N.; Khusainova, N. G.; Ageeva, A. G. *Zh. Obshch. Khim.* **1964**, *34*, 3938–3942.
7. Maerkl, G.; Merkl, B. *Tetrahedron Lett.* **1983**, *24*, 5865–5868.
8. Portnoy, N. A.; Morrow, C. J.; Chatta, M. S.; Williams, J. C.; Aguiar, Jr., A. M. *Tetrahedron Lett.* **1971**, 1397–1400.
9. Rousselet, G.; Capdeville, P.; Maumy, M. *Tetrahedron Lett.* **1993**, *34*, 6395–6398.
10. Kazankova, M. A.; Trostyanskaya, I. G.; Lutsenko, S. V.; Beletskaya, I. P. *Tetrahedron Lett.* **1999**, *40*, 559–572.
11. Karplus, M. *J. Chem. Phys.* **1959**, *30*, 11.
12. Petrov, A. A.; Ionin, B. I.; Ignat'ev, V. M. *Tetrahedron Lett.* **1968**, 15–16.
13. Timofeeva, T. N.; Ignat'ev, V. M.; Ionin, B. I.; Petrov, A. A. *Dokl. Akad. Nauk SSSR* **1969**, *189*, 1052–1054.
14. Palocios, F.; Aparicio, D.; Garcia, J. *Tetrahedron* **1996**, *52*, 9609–9628.
15. Palocios, F.; Ochoa de Retana, A.na M. *Tetrahedron* **1999**, *55*, 3091–3104.
16. Duncan, M.; Gallagher, M. J. *Org. Magn. Res.* **1981**, *15*, 37–42.
17. Richard, J. J.; Banks, C. V. *J. Org. Chem.* **1963**, *28*, 123.