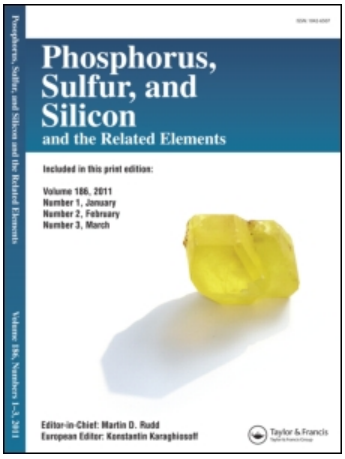

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Dichlorodimethyl Hydantoin: An Efficient Reagent for One-Pot Synthesis of CWC-Related O,O-dialkyl, N,N-dialkyl Phosphoramidates

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A simple, rapid, economical, and efficient one-pot synthetic method for preparation of O,O-dialkyl, N,N-dialkylphosphoramidates (DADAPs) and phosphates has been developed.

Keywords CWC; dichlorodimethyl hydantoin; O,O-dialkyl, N,N-dialkylphosphoramidates; phosphates

INTRODUCTION

Development of efficient synthetic procedures for retrospective detection and identification of chemical warfare agents (CWAs) and related compounds is a prominent area of research that has attracted the attention of several workers due to the strict verification program of Chemical Weapons Convention (CWC).[1–6] The convention entered into the force on 29 April 1997 and prohibits the development, production, stockpiling and use of chemical weapons. By April 2006, 176 countries had ratified the convention. An international organization, known as the Organisation for the Prohibition of Chemical Weapons (OPCW) ensures implementation of CWC by implementing the verification program. Verification involves collection of samples from production, storage and suspected sites by inspectors appointed by the OPCW.[7] Inspectors perform on-site analysis of collected samples to detect and identify CWC related chemicals. Where there is ambiguity, the samples are sent to at least two off-site laboratories designated by the OPCW for unambiguous identification of the CWC related chemicals.[7,8] Thus, a laboratory willing to undertake the challenging task of off-site analysis of such chemicals

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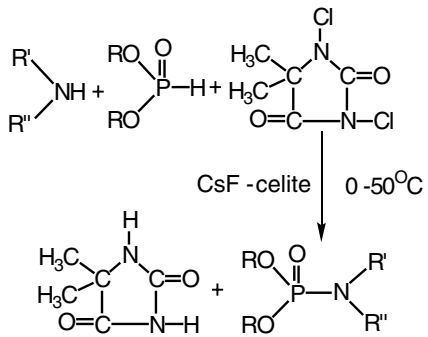
for verification should first achieve the status of 'designated laboratory' from the OPCW. Laboratories become and stay designated by proving their analytical capability in Official Proficiency Tests (OPTs) conducted by the OPCW.[9,10] The performance of participating laboratory in OPTs mainly depends on availability of spectral data of CWC-related chemicals, sample preparation, analytical skills of chemists, judgment and reporting.

Schedules of compounds are based on commercial use and alleged use of chemicals as CWAs.[8] As the total number of scheduled compounds is several million,[7,8] their synthesis (in pure form) by reported methods and the recording of spectral data base is a daunting task. To overcome such problems, there is an urgent need to develop efficient and rapid synthetic procedures, which provide the pure compounds with minimal work up. Rapid synthesis of these compounds in pure form is also required to report the correct formula of isomeric compounds by overlapping their spectra with the GC-MS and ^{31}P NMR spectra of spiked compounds.. The perfect match of test sample spectra with synthesized compounds is one of the unique ways to report the results of analysis as it does not require much expertise in the field of interpretation of spectra.[9,11–14] *O*-alkyl N,N-dialkylphosphoramidocyanidates (ADAPCs) are analogues of highly toxic nerve agent tabun (*O*-ethyl N,N-dimethyl phosphoramidocyanidate) and fall in Schedule 1.A.2 of the CWC Annex.[7] Based on commercially available C_1-C_{10} alcohols, the estimated number of compounds belonging to Schedule 1.A.2 is 48,000 and their corresponding *O*,*O*-dialkyl, *N*,*N*-dialkyl phosphoramidates (DADAPs) are often produced when tabun or its derivatives are produced in laboratories or chemical plants.[8] Hence, DADAPs are important chemical markers because of their stability and persistency in the environment and their confirmed presence provides evidence for the presence of tabun and related compounds for verification. Because of this property DADAPs, appear in Schedule 2 B6 category of CWC and probably this the reason they are quite often used in Official Proficiency Test (12, 14, and 18 tests). This fact prompted us to develop an efficient one-pot synthesis of phosphoramidates from dialkyl phosphites. A plethora of effective chemical approaches have been devised for the preparation of phosphoramidates.[15–25] However, these methods suffer from several draw backs such as non-availability of intermediates (*N*,*N*-dialkylphosphoramidic dichlorides), requires an additional step, time consuming, poor atom economy (requires extra equivalents of base as acid scavenger), and use of organic solvents. The reaction is also performed at high temperature 240°C resulting in tar formation, which reduces the yields of the desired products.[3,25]

Recently, there has been increasing emphasis on finding out low moleculer weight recyclable environmentally friendly reagents.[26] This is essentially required to reduce the amount of toxic waste and by-products arising from a chemical process.[27] One such reagent is *N*,*N*′-dichlorodimethyl hydantoin (DCDMH) a cheap, commercially available reagent and recently used as an excellent reagent for deoximation of ketones, preparation of *gem*- chloro nitroso alkanes, nitrosation of amines and in neutralization of chemical warfare agents,[28] and also has two positive chlorine.

In continuation of our earlier work,[29,30] we report a rapid, efficient, economic, and easy to scale-up method for the effective one pot conversion of dialkyl phosphites to their corresponding phosphoramidates at moderate temperature using DCDMH (non toxic and commercially available reagent) followed by addition of dialkylamines. To investigate the simplicity and effective transformation of phosphoramidates via *in-situ* generation of dialkyl chlorophosphates approach (Scheme 1) was followed. The phosphites were reacted with DCDMH to generate dialkyl chlorophosphate followed by phosphorylation reactions with various dialkyl amines in presence of CsF-celite at 0°C without isolating the intermediate (dialkyl chlorophosphates).



SCHEME 1

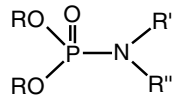
The results of this study indicates, that the work-up procedure of reaction of dialkyl phosphites 1 and DCDMH 2 was simple and suitable for the preparation DADAPAs due to easy removal of by-product dimethyl hydantoin (DMH) from the reaction mixture as it is insoluble in diethyl ether and DADAPAS are soluble in ether. In order to optimize the mole ratio, various reactions were carried out and the optimum yield was obtained when a reaction was carried out in 1: 0.5: 2:1 molar ratios of dialkyl phosphite, DCDMH, CsF-celite, and dialkylamines, respectively. It is important to note that CsF-celite should be added first and

dialkylamines should be added later at 0°C slowly to the stirred reaction mixture. The desired phosphoramidates were obtained in excellent yield with exceptionally high purities (Scheme 1 and Table I). To find out effectiveness of CsF-celite,[31] a model reaction between diisopropyl phosphite and DCDMH was performed with various solid supports such as anhydrous sodium sulfate, silica, charcoal, active carbon, CsF, celite, and basic alumina, followed by the addition of diethylamine. Combination of CsF-celite gave better results in terms of reduced reaction time, isolation of pure product and yield of the product.

It was observed that when CsF alone was used as a solid support, unreacted diisopropyl fluorophosphate (DFP) along with tetra isopropyl pyrophosphate was found (^{31}PNMR and GC-MS analysis). It indicated that isolation of pure product became difficult from contaminated fluorophosphates. Furthermore, to examine the role of CsF-celite, a control experiment was performed except in the absence of CsF-celite and monitored by GC and ^{31}P NMR after drawing few milligrams sample and washed with diethyl ether. The results of ethereal solution analysis showed that the formation of DADAPAs was invariably poor (15–25% only) and contaminated with corresponding unreacted dialkyl chlorophosphate as a major product and an unidentified product (5–10%) in each case. The poor yield of DADAPAs can be explained by consumption of same amine to form their corresponding hydrochloride salt. Furthermore, in the absence of CsF-celite, these reactions required longer reaction times for completion of the reaction. Most probably CsF-celite brought the reactants closure to each other which enhances the reactivity on the surfaces and facilitated the reactions.[31] To study the applicability of DCDMH, various reactions of diethylphosphite and diethylamine in absence of DCDMH but in presence CsF-celite under neat conditions were also performed by varying the mole ratio and temperature, but there was no formation of corresponding diethyl, N,N-diethylphosphoramidate on TLC. It indicated that DCDMH is generating the corresponding dialkyl chlorophosphate which subsequently reacting with dialkylamines in presence of CsF-celite.

In order to study the effect of substituents, various reactions of different dialkyl phosphites were performed with diethyl amine in presence of DCDMH and CsF-celite under identical reaction conditions. We observed that the reaction of dimethyl phosphite and diethyl amine in presence of DCDMH and CsF-celite completed within 35 min and corresponding phosphoramidates were obtained in 84% yield. However, phosphorylation of diisopropyl phosphite with diethyl amine was relatively slow and took 50 min under same reaction conditions. It indicated that, as the size of alkyl group of dialkylphosphite increases, the reactivity of diethyl amine decreased. Furthermore, to study the

TABLE I One-Pot Synthesis of O,O-dialkyl, N,N′-dialkyl Phosphoramidates from Dialkylphosphites, DCDMH and Dialkyl Amine in Presence of CsF-celite



Entry	R	R′	R″	Time (min)	Temp (°C)	Yield[a](%)
1	CH_3	CH_3	CH_3	20	25	89
2	CH_3	C_2H_5	C_2H_5	20	35	84
3	CH_3	*n*-C_3H_7	*n*-C_3H_7	35	35	83
4	CH_3	*i*-C_3H_7	*i*-C_3H_7	40	40	86
5	CH_3	CH_3	C_2H_5	20	25	86
6	CH_3	*n*-C_3H_7	C_2H_5	25	25	85
7	CH_3	*i*-C_3H_7	C_2H_5	30	30	86
8	CH_3	*n*-C_3H_7	CH_3	25	30	82
9	CH_3	*i*-C_3H_7	*n*-C_3H_7	30	50	87
10	CH_3	*i*-C_3H_7	CH_3	25	30	85
11	C_2H_5	CH_3	CH_3	25	30	82
12	C_2H_5	C_2H_5	C_2H_5	40	35	80
13	C_2H_5	*n*-C_3H_7	*n*-C_3H_7	30	35	88
14	C_2H_5	*i*-C_3H_7	*i*-C_3H_7	50	50	83
15	C_2H_5	CH_3	C_2H_5	25	30	88
16	C_2H_5	*n*-C_3H_7	C_2H_5	25	30	84
17	C_2H_5	*i*-C_3H_7	C_2H_5	40	35	81
18	C_2H_5	*n*-C_3H_7	CH_3	30	30	80
19	C_2H_5	*i*-C_3H_7	*n*-C_3H_7	45	30	82
20	C_2H_5	*i*-C_3H_7	CH_3	25	35	84
21	*n*-C_3H_7	CH_3	CH_3	30	30	88
22	*n*-C_3H_7	C_2H_5	C_2H_5	30	30	86
23	*n*-C_3H_7	*n*-C_3H_7	*n*-C_3H_7	40	40	84
24	*n*-C_3H_7	*i*-C_3H_7	*i*-C_3H_7	65	50	84
25	*n*-C_3H_7	CH_3	C_2H_5	30	30	82
26	*n*-C_3H_7	*n*-C_3H_7	C_2H_5	30	30	84
27	*n*-C_3H_7	*i*-C_3H_7	C_2H_5	50	40	84
28	*n*-C_3H_7	*n*-C_3H_7	CH_3	30	30	85
29	*n*-C_3H_7	*i*-C_3H_7	*n*-C_3H_7	65	40	87
30	*n*-C_3H_7	*i*-C_3H_7	CH_3	35	30	82
31	*i*-C_3H_7	CH_3	CH_3	40	30	82
32	*i*-C_3H_7	C_2H_5	C_2H_5	50	40	83
33	*i*-C_3H_7	*n*-C_3H_7	*n*-C_3H_7	50	50	80
34	*i*-C_3H_7	*i*-C_3H_7	*i*-C_3H_7	90	60	80
35	*i*-C_3H_7	CH_3	C_2H_5	30	35	81
36	*i*-C_3H_7	*n*-C_3H_7	C_2H_5	60	35	83
37	*i*-C_3H_7	*i*-C_3H_7	C_2H_5	35	40	82
38	*i*-C_3H_7	*n*-C_3H_7	CH_3	40	35	84
39	*i*-C_3H_7	*i*-C_3H_7	*n*-C_3H_7	75	50	85
40	*i*-C_3H_7	*i*-C_3H_7	CH_3	45	35	80

[a]Reactions were monitored by ^{31}P NMR in $CDCl_3$ at 162 MHz, and the products had satisfactory I.R, NMR and Mass data; GC-MS data were compared with literature values.[32]

effect of various amines with in situ formed dialkyl chlorophosphates, we found that reaction of dimethyl amine completed more quickly than ethyl methyl amine. We also noticed that by increasing the size of chain length, the reactivity of these amines decreased. However, diisopropyl amine somewhat took little longer time (40–90 min) in each case. The reaction of diisopropyl phosphite and diisopropyl amine was slowest and took maximum time (90 min). It is essentially due to presence of sterically hindered diisopropyl amino group in both substrate and reagent, which might have reduced the reactivity.

The positive feature of this method is that the product can be obtained simply by filtration. The filtrate contains the desired products and residue after washings with sufficient acetone can be recycled for the preparation of DCDMH. The solid residue can be reused after activating it in oven at 150°C for 2 h. The important advantage of this method is minimum use of solvent, easy work up, and its occurrence at mild temperatures. In terms of atom economy, it does not require extra base to scavenge HCl. Another advantage is that the by-product DMH is not reacting with amines under these conditions. To examine the reproducibility of one-pot concept at higher mole ratio, 200 mmol of diethyl phosphite was reacted with 10.0 mmol of the reagent DCDMH in diethyl ether at room temperature. The reaction mixture was stirred for 15 min and monitored by ^{31}P NMR; it showed complete conversion of the diethyl phosphite to the corresponding diethyl chlorophosphate within 15 min The CsF-celite was added followed by the slow addition of ethyl methyl amine (0.1mol) in the heterogeneous reaction mixture at 0°C. The reaction mixture was stirred on vortex shaker for the period given in Table I and periodically monitored by ^{31}P NMR by drawing few milligram of sample from the reaction mixture. The results of NMR studies indicated that signal of diethyl chlorophosphate at δ 4.14 completely disappeared and a new signal appeared at δ 13.58 clearly demonstrated that the rapid conversion of diethyl chlorophosphate to the corresponding O,O-diethyl, N-ethyl, N-methylphosphoramidates. Filtration of heterogeneous reaction mixture and concentration of the solvent provided the pure product in 88% isolated yield.

CONCLUSIONS

In conclusion, we have developed a simple, rapid, economical and efficient one-pot synthetic method for the preparation of DADAPs and the phosphates. The method is very useful for spectral up-gradation for CWC verification and for the synthesis of biologically active compounds. The method can be extended for the synthesis of various pseudo phosphates. Thus, it will make a useful and an important addition to

existing methodologies. In addition to this, the recycling of the reagent, and the easy and clean work-up with high yields, makes this an attractive methodology. Further, the application of DCDMH in the synthesis of various organic compounds is in progress and will be reported in due course.

EXPERIMENTAL

IR spectra were recorded on Bruker FT-IR spectrometer model Tensor 27 on KBr disk. ^{1}H and ^{31}P NMR spectra were recorded on Bruker DPX Avance FT- NMR in $CDCl_3$ using tetramethylsilane as an internal standard for ^{1}H and 85% H_3PO_4 as an external standard for ^{31}P NMR at 400 and 162 MHz, respectively. A Chemito GC model 1000 instrument was used with flame ionization detector (FID). A capillary column (30 m $\times$ 0.25 mm I.D-BP5) packed with 5% phenyl and 95% dimethyl polysiloxane (SGE) coated on fused silica was employed. The injection port and detector block were maintained at 280°C and 260°C respectively and the column oven was at programmed temperature profile started at 50°C, ramped up to 280°C at 25°C/min Nitrogen was used as a carrier gas (at a flow rate of 30ml/min). Air for FID was supplied at 300ml/min and hydrogen at 30ml/min In all analyses, 1μl sample was injected and peaks were recorded on computerized data acquisition station. The GC-MS analyses were performed in EI (70 eV) in full scan mode with an Agilent 6890 GC equipped with a model 5973 mass selective detector (Agilent Technologies, USA). An SGE BPX5 capillary column with 30 m length $\times$ 0.32 mm internal diameter $\times$ 0.25 μm film thickness was used at temperature program of 80°C (2 min)-20°C/min-280°C (3 min). Helium was used as the carrier gas at a constant flow rate of 1.2 ml/min. The samples were analyzed in splitless mode at injection temperature of 250°C, EI source temperature 230°C and quadrupole analyzer at 150°C.

Preparation of Solid-Surface Material CsF-Celite

The preparation of CsF-Celite substance was carried out in the same manner as we described in literature.[33] 152 g (1000 mmol) of cesium fluoride was added to a solution of 100g (1660 mmol) of Celite@ 521 in 1000 ml of distilled water. This heterogenous mixture was stirred for 1 h at room temperature and then water was removed under vacuum using Heidolph rotary evaporator until dry It was shaken with 3 $\times$ 100 ml acetonitrile, filtered and washed with 3 $\times$ 25 ml acetonitrile. The CsF-Celite substance was dried under vacuum and stored in desiccators.

General Experimental Procedure

In a typical experimental procedure, dialkylphosphite (50.0 mmol) was added in suspended solution of DCDMH (4.92 g, 25.0 mmol) in 15 ml acetonitrile and reaction mixture was stirred for 10–30 min. The progress of the reaction mixture was monitored by ^{31}P NMR by drawing a few milligrams of reaction mixture to find out the consumption of dialkyl phosphite. A white amorphous precipitate of DMH **4** was formed. When precipitation of **four** ceased, reaction mixture was cooled at 0^0 C, solvent was removed under reduced pressure at r.t. and CsF-celite (25.32 g, 100 mmol CsF and 160 mmol of Celite) mole was added. The dialkylamine (50.0 mmol) was added slowly with shaking in heterogeneous reaction mixture on a vortex shaker. The progress of the reaction was further monitored by ^{31} P NMR to find out the consumption of dialkyl chlorophosphate by drawing a few milligrams of reaction mixture after extracting with ether. After completion of reaction (as time and temperature mentioned in Table I), reaction mixture was extracted with ether and a white solid substance (mixture of **4** and solid support) was removed by filtration and washed with acetonitrile (3x10 ml). The solvent was removed from the filtrate and the product was distilled under vacuum to get pure DADAPs.

Dimethyl–N,N-dimethylphosphoramidate

Bp: 82–83°C (6 mmHg); ^{31}P NMR (161.98 MHz, $CDCl_3$): $\delta = 14.07$.^{1}H-NMR (400.13 MHz, $CDCl_3$): $\delta = 3.72$(d, 6H, OCH_3 $J_{H\text{-}P} = 12.0$Hz), 2.9(d, 6H, N-CH_3). IR: Neat (KBr) υ(max): 2972, 2899, (C—H Str.), 1380(C—H bend), 1272(P═O), 1160(P-N-C), 1090, 1050(P-O-C) cm^{-1}. MS (EI): m/z (%) = 153(21), 120(20), 109 (39), 79(15), 44 (100).

Dimethyl-N, N-diethylphosphoramidate

Bp: 98–99°C (5 mmHg); ^{31P}NMR (161.98 MHz, $CDCl_3$): $\delta = 13.57$. ^{1}H-NMR ($CDCl_3$): $\delta = 3.75$ (d, 6H, OCH_3 $J_{H\text{-}P} = 12.0$ Hz), 3.3(m,4H,-CH_2N-), 1.2(t,6H,CH_3-). IR: (Neat) (KBr) υ (max): 2943, 2989(C—H str.), 1385 C—H bend), 1268 (P═O), 1163 (P-NC), 1090, 1050(P-O-C) cm^{-1}. MS (EI): m/z (%) = 181(10), 166(100), 138 (33), 109(45), 72 (15).

Dimethyl-N, N-dipropylphosphoramidate

Bp: 92–93°C (2 mmHg); ^{31}P NMR (161.98 MHz, $CDCl_3$): $\delta = 13.81$. ^{1}H-NMR ($CDCl_3$): $\delta = 3.78$ (d, 6H, OCH_3, $J_{H\text{-}H} = 12.0$ Hz), 3.3 (m, 4H,-CH_2-N-), 1.75(m, 4H, -CH_2-), 1.0 (t, 3H, CH_3) . IR: (neat) (KBr) υ (max): 2978, 2947, 2889 (C—H str.), 1385 (C—H bend), 1262(P═O), 1167 (P-N-C), 1080, 1040(P-O-C) cm^{-1}. MS (EI): m/z (%) = 209(4), 194(68), 152 (100), 166(17), 109 (33) 79 (17).

Dimethyl-N, N- diisopropylphosphoramidate

Bp: 95–96°C (3 mmHg); ^{31}P NMR (161.98 MHz, $CDCl_3$): $\delta = 11.51$. ^{1}H-NMR ($CDCl_3$): $\delta = 3.80$ (d,6-H,OCH_3 $J_{H\text{-}H}$ =12.0 Hz), 3.4(m, 2H,-CH-), 1.4 (d, 12H, CH_3). IR (neat) (KBr) υ (max): 2977, 2940, 2896 (C—H str), 1382 (C—H bend), 1275 (P═O), 1174(P-N-C),1090,1050 (P-O-C)cm^{-1}. MS(EI):m/z(%) = 209 (4), 194(68), 152(100), 166(17), 109(33), 79(17).

Dimethyl-N-ethyl-N-methylphosphoramidate

Bp: 83–85°C (5 mmHg); ^{31}P NMR (161.98 MHz, $CDCl_3$): $\delta =$ 13.87.^{1}H-NMR ($CDCl_3$): $\delta = 3.78$ (d,6-H,OCH_3 $J_{H\text{-}H}$ = 12.0Hz), 3.25 (m,2H,-CH_2-), 2.75(d,3H, N-CH_3), 1.5 (t,3H,CH_3).IR: (neat) (KBr) υ (max): 2970, 2945, (C—H str), 1382 (C—H bend), 1273(P═O), 1174(P-N-C), 1090, 1050 (P-O-C)cm^{-1}. MS (EI): m/z (%) = 167(12), 152(100),122(45), 109(67), 79 (13).

Dimethyl-N-ethyl-N-propylphosphoramidate

Bp: 93–95°C (3 mmHg); ^{31}P NMR (161.98 MHz, $CDCl_3$): $\delta = 13.75$. ^{1}H-NMR ($CDCl_3$): $\delta = 3.80$ (d, 6-H, OCH_3 $J_{H\text{-}H} = 12.0$ Hz), 3.25 (m,4H,-CH_2-N-), 1.55 (m,2H,-CH_2-)1.15(t,3H,CH_3-), 0.88(t,3H, CH_3-).IR: (neat) (KBr) υ(max): 2977, 2950, (C—H Str), 1387(C—H bend), 1272 (P═O), 1160(P-N-C), 1090, 1050(P-O-C) cm^{-1}. MS (EI): m/z (%) = 195(5), 166(100), 138 (44), 109(36), 79 (11).

Dimethyl-N-ethyl-N- isopropylphosphoramidate

Bp: 84–86°C (4.5 mmHg); ^{31}P NMR (161.98 MHz, $CDCl_3$): $\delta = 11.17$. ^{1}H-NMR ($CDCl_3$): $\delta = 3.79$ (d,6-H, OCH_3 $J_{H\text{-}H}$ = 12.0 Hz), 3.9(m,1H,-CH-), 3.20 (m,2H,-CH_2-), 1.25 (t,3H,CH_3), 1.2(d,6H,CH_3-).IR: (neat) (KBr) υ (max): 2975, 2947, (C—H str), 1380 (C—H bend), 1267 (P═O), 1167 (P-N-C),1090,1050 (P-O-C) cm^{-1}. MS (EI): m/z (%) = 195(4), 180(100), 138 (52), 152 (67), 120 (24), 109 (46), 79 (20)

Dimethyl-N-methyl-N- propylphosphoramidate

Bp: 98–99°C (6 mmHg); ^{31}P NMR (161.98 MHz, $CDCl_3$): $\delta = 13.72$. ^{1}H-NMR ($CDCl_3$): $\delta = 3.80$ (d,6-H, OCH_3 $J_{H\text{-}H}$ = 12.0Hz), 3.1 (m, 2H, -CH_2-N), 2.75 (d,3H,CH_3-N)1.55(m,2H,-CH_2-), 0.89(t,3H, CH_3-). IR: (neat) (KBr) υ (max): 2976, 2953 (C—H str.), 1382 (C—H bend), 1265 (P═O), 1174 (P-N-C), 1085, 1045 (P-O-C) cm^{-1}. MS (EI): m/z (%) = 181(8), 152(100), 122 (45), 109(51), 79, (11), 42(20).

Dimethyl-N-propyl-N-isopropylphosphoramidate

Bp: 98-99°C (2 mmHg); ^{31}P NMR (161.98 MHz, $CDCl_3$): $\delta = 11.17$. ^{1}H-NMR ($CDCl_3$): $\delta = 3.80$ (d, 6-H, OCH_3 $J_{H\text{-}H}$ = 12.0 Hz), 3.6(m, 1H,-CH-), 3.21(m,2H,-CH_2-N-),1.6(m,2H,-CH_2-),1.2(d,6H,CH_3-), 0.88 (t, 3H,

CH_3-).IR: (neat) (KBr) υ (max): 2976, 2953 (C—H str.), 1375(C—H bend), 1266(P=O), 1165(P-N-C), 1090, 1050(P-O-C) cm^{-1}.MS (EI): m/z (%) = 209(2), 194(47), 180, (54), 166 (12), 152(43), 138 (100), 109 (31), 79 (11).

Dimethyl-N-methyl-N-sopropylphosphoramidate

Bp: 88–89°C (6 mmHg); ^{31}P NMR (161.98 MHz, $CDCl_3$): $\delta = 11.19$. ^{1}H-NMR ($CDCl_3$): $\delta = 3.80$ (d, 6-H, OCH_3 $J_{H\text{-}H} = 12.0$ Hz), 3.75 (m, 1H, -CH-) 2.73(d, 3H, CH_3-N-),1.15(d, 6H,CH_3).IR: (neat) (KBr) υ(max): 2980, 2955, (C—H str),1372 (C—H-bend), 1272(P=O), 1168(P-NC), 1090, 1055(P-O-C) cm^{-1}.MS (EI): m/z (%) = 181(2), 166(100), 136 (4), 134 (16), 109(27), 79 (11), 56 (42), 42 (16).

Diethyl-N, N-dimethylphosphoramidate

Bp: 82–83°C (5 mmHg); ^{31}P NMR (161.98 MHz, $CDCl_3$): $\delta = 11.45$. ^{1}H-NMR ($CDCl_3$): $\delta = 4.25$(m, 4-H, -OCH_2, J_{H-H} =7.0 $J_{H\text{-}P} = 8.0$ Hz), 2.79(d, 6H, N-CH_3), 1.33(t, 6-H, -CH_3 $J_{H\text{-}H} = 7.0$ Hz). IR: (neat) (KBr) υ (max): 2972, 2899, (CH Str.), 1380 (C—H bend), 1267(P=O), 1160(P-N-C), 1090, 1053(P-O-C) cm^{-1}.MS (EI):m/z (%) = 181(18),152(6),136 (6),124(34),109(5), 111(11),110(12),108(38),44(100).

Diethyl-N, N-diethylphosphoramidate

Bp: 109–110°C (1 mmHg); ^{31}P NMR (161.98 MHz, $CDCl_3$): $\delta =$ 10.87. ^{1}H-NMR($CDCl_3$): $\delta = 4.25$(m,4-H,-OCH_2,$J_{H\text{-}H} = 7.0$ $J_{H-P} = 8.0$ Hz),3.3(m, 4H,-CH_2-), 1.33 (t, 6-H, CH_3 $J_{H\text{-}H} = 7.0$Hz), 1.2 (t, 6H, CH_3-), IR: (neat) (KBr) υ(max): 2943, 2989(C—H str.), 1385 C—H bend), 1268 (P=O), 1163 (P-NC), 1085,1052 (P-O-C) cm^{-1}. MS (EI): m/z (%) = 209(12), 194(74), 180, (6), 166 (37), 152(16), 138 (100), 110 (39),72 (17).

Diethyl-N, N-dipropylphosphoramidate

Bp: 110–111°C (2 mmHg); ^{31}P NMR (161.98 MHz, $CDCl_3$): $\delta =$ 11.09. ^{1}H-NMR ($CDCl_3$): $\delta = 4.25$(m,4-H,-OCH_2, $J_{H\text{-}H} = 7.0$ $J_{H-P} =$ 8.0 Hz),3.3(m,4H,-CH_2-N-),1.75 (m,4H,-CH_2-), 1.33(t,6-H, CH_3 $J_{H\text{-}H} =$ 7.0 Hz),1.0(t,6H,CH_3); IR: (neat) (KBr) υ(max):2975,2947,2883(C—H str.), 1362, 1270(P=O),1166(P-N-C),1080,1040 (P-O-C)cm^{-1}.MS (EI): m/z (%) = 237(8), 222(47), 180(31), 152(23), 138(100), 110(29), 72(21).

Diethyl-N,N-diisopropylphosphoramidate

Bp: 116–117°C (1 mmHg); ^{31}P NMR (161.98 MHz, $CDCl_3$): $\delta = 8.80$. ^{1}H-NMR ($CDCl_3$): $\delta = 4.25$(m,4-H, -OCH_2, $J_{H\text{-}H}$ =7.0 $J_{H-P} = 8.0$ Hz), 3.4(m,2H,-CH-), 1.4(d,12H,CH_3-), 1.31(t,6-H, CH_3 $J_{H\text{-}H}$ =7.0Hz). IR: (neat) (KBr) υ(max): 2978, 2945, 2893 (C—H str), 1380(C—H bend),

1170(P-N-C), 1275, (P═O),1088, 1045 (P-O-C) cm^{-1}. MS (EI): m/z (%) = 237(4), 222(10), 180(11), 138(100), 110(16), 72(13).

Diethyl-N-ethyl-N-methylphosphoramidate

Bp: 109–110°C (1 mmHg); ^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 10.77. ^1H-NMR ($CDCl_3$): δ = 4.25(m,4-H,-OCH_2,$J_{H\text{-}H}$ =7.0J_{H-P} =8.0Hz),3.25(m,2H,-CH_2-), 2.75 (d,3H,CH_3),1.5(t,3H,CH_3),1.33(t,6-H,$CH_3J_{H\text{-}H}$ =7.0Hz). IR: (neat) (KBr) υ(max): 2973, 2944, (C—H str), 1379(C—H bend.) 1267(P═O), 1165(P-N-C), 1087, 1048(P-O-C) cm^{-1}. MS (EI): m/z (%) = 195(13), 180(74), 152(40), 138 (12), 124 (100), 110(11), 58 (35).

Diethyl-N-ethyl-N-propylphosphoramidate

Bp: 121–122°C (1 mmHg); ^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 11.06. ^1H-NMR ($CDCl_3$): δ = 4.25(m,4-H, -OCH_2, $J_{H\text{-}H}$ =7.0 J_{H-P} =8.0Hz),3.26(m,4H,-CH_2-N-), 1.54(m,2H,-CH_2-),1.34(t,6-H,-CH_3 $J_{H\text{-}H}$ = 7.0Hz),1.14 (t,3H, CH_3-), 0.89(t,3H, CH_3-).IR: (neat) (KBr) υ(max): 2978, 2954, (C—H Str), 1385(C—H bend),1266(P═O), 1164(P-N-C), 1091,1047(P-O-C) cm^{-1}.MS (EI): m/z (%) = 233(3), 208(7), 194 (100), 180 (5), 166 (45), 152(9), 138 (82), 110 (39), 86 (7).

Diethyl-N-ethyl-N-isopropylphosphoramidate

Bp: 92–93°C (10 mmHg); ^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 8.66. ^1H-NMR ($CDCl_3$): δ = 4.23(m,4-H, -OCH_2, $J_{H\text{-}H}$ =7.0 J_{H-P} =8.0Hz),3.91(m,1H,-CH-), 3.21 (m, 2H,-CH_2-), 1.33(t,6-H,-CH_3 $J_{H\text{-}H}$ = 7.0Hz), 1.21 (d,6H, CH_3-), 1.24(t,3H,-CH_3).IR: (neat) (KBr) υ(max): 2975, 2947, (C—H stn), 1380 (C—H bend),1267 (P═O), 1167 (P-N-C), 1090,1050(P-O-C) cm^{-1}.MS (EI): m/z (%) = 233(4), 208(100), 180 (35), 152 (92), 166 (21),152(90), 138 (12), 124 (25), 110 (21), 86 (11).

Diethyl-N-methyl-N-propylphosphoramidate

Bp: 81–82°C (1 mmHg); ^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 11.02. ^1H-NMR ($CDCl_3$): δ = 4.25(m,4-H, -OCH_2, $J_{H\text{-}H}$ =7.0 J_{H-P} =8.0 Hz), 3.1(m,2H,-CH_2-N), 2.75(d,3H,CH_3-N) 1.55(m,2H,-CH_2-), 1.33(t,6-H, -CH_3 $J_{H\text{-}H}$ =7.0Hz), 0.89(t,3H, -CH_3).IR: (neat) (KBr) υ(max): 2976, 2953 (C—H str.), 1375(C—H bend), 1265(P═O), 1174(P-N-C), 1085, 1045(P-O-C) cm^{-1}. MS (EI): m/z (%) = 209(7), 208( ), 180 (85), 152(41), 124 (100), 110 (5), 72 (14).

Diethyl-N-propyl-N-isopropylphosphoramidate

Bp: 95–96°C (1 mmHg); ^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 11.57. ^1H-NMR ($CDCl_3$): δ = 4.25(m,4-H, -OCH_2, $J_{H\text{-}H}$ = 7.0 J_{H-P} = 8.0 Hz),

3.6(m,1H,-CH-), 3.1(m,2H,CH_2-N-), 1.6(m,2H,-CH_2-), 1.33(t,6-H, -CH_3 $J_{H\text{-}H}$ = 7.0Hz), 1.2(d,6H,CH_3-), 0.88(t,3H,CH_3-).IR: (neat) (KBr) υ(max): 2976, 2953 (C—H str.), 1375(C—H bend), 1266(P═O), 1165(P-N-C), 1090, 1050(P-O-C) cm^{-1}. MS (EI): m/z (%) = 237(3), 222 (38), 208 (87), 194(17),180 (13), 166 (100), 152(57), 124 (26), 100 (9).

Diethyl-N-methyl-N- isopropylphosphoramidate

Bp: 98–990°C (0.5 mmHg); ^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 10.77. ^{1}H-NMR ($CDCl_3$): δ = 4.25(m,4-H, -OCH_2, $J_{H\text{-}H}$ =7.0 J_{H-P} =8.0 Hz), 3.75(m, 1H, -CH-) 2.65(d,3H,CH_3-N-), 1.33(t,6-H, -CH_3 $J_{H\text{-}H}$ = 7.0Hz), 1.15(d,6H,CH_3).IR: (neat) (KBr) υ(max): 2980, 2955, (C—H str), 1372(C—H-bend), 1273(P═O), 1168(P-NC), 1090, 1050(P-O-C) cm^{-1}.MS (EI): m/z (%) = 209(3), 194(7), 166 (25), 138 (100), 124 (60), 120 (15), 72 (11).

Diproyl-N,N-dimethylphosphoramidate

Bp: 92–93°C (3 mmHg); ^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 11.51.^{1}H-NMR ($CDCl_3$): δ = 4.05(m,4-H, -OCH_2, $J_{H\text{-}H}$ = 7.0 J_{H-P} =8.0 Hz), 2.9(d,6H, -NCH_3), 1.74(m, 4H, -CH_2), 0.97(t,6-H, -CH_3 $J_{H\text{-}H}$ = 7.0Hz);IR: (neat) (KBr) υ(max): 2972, 2899, (CH Str.), 1380, (C—H bend), 1272(P═O), 1160(P-N-C), 1090,1050(P-O-C) cm^{-1}. MS (EI): m/z (%) = 209(3), 168 (20), 150(7), 138 (100), 126 (63), 124 (33),108 (31), 44 (100).

Diproyl-N,N-diethylphosphoramidate

Bp: 119–120°C (1 mmHg); ^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 10.27. ^{1}H-NMR ($CDCl_3$): δ = 4.05(m,4-H, -OCH_2, $J_{H\text{-}H}$ = 7.0 J_{H-P} =8.0 Hz), 3.3(m,4H,-CH_2-), 1.74(m, 4H, CH_2),1.2(t,6H,CH_3-), 0.97(t,6-H, -CH_3 $J_{H\text{-}H}$ = 7.0Hz);IR: (neat) (KBr) υ(max): 2943, 2989(C—H str.), 1385 (C—H bend), 1268 (P═O), 1163 (P-NC), 1090,1050(P-O-C) cm^{-1}. MS (EI): m/z (%) = 237(3), 222(42), 180 (25), 138 (100), 124(12), 110 (19),72 (25).

Dipropyl-N,N-dipropylphosphoramidate

Bp: 113–114°C (1 mmHg); ^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 11.22. ^{1}H-NMR ($CDCl_3$): δ = 4.05(m,4-H, -OCH_2, $J_{H\text{-}H}$ = 7.0 J_{H-P} =8.0 Hz), 3.3(m,4H,-CH_2-N-), 1.72- 1.76 (m, 8H, -CH_2-), 1.02(t,3H,CH_3), 0.97(t,6-H, -CH_3 $J_{H\text{-}H}$ = 7.0Hz); IR: (neat) (KBr) υ(max): 2978, 2947, 2889 (C—H str.), 1365, (C—H bend), 1262(P═O), 1167(P-N-C), 1080,1040(P-O-C) cm^{-1}. MS (EI): m/z (%) = 265(2), 236(67), 194 (30), 152(100), 134 (11) 138 (8), 110 (45), 100 (9).

Dipropyl-N,N-diisopropylphosphoramidate

Bp: 123–124°C (1 mmHg); ^{31}P NMR (161.98 MHz, $CDCl_3$): $\delta = 8.90$. ^{1}H-NMR ($CDCl_3$): $\delta = 4.05$(m,4-H, -OCH_2, $J_{H\text{-}H} = 7.0$ J_{H-P} =8.0 Hz), 3.4(m,2H,-CH-), 1.74(m, 4H, CH_2),1.4(d,12H,CH_3-),0.97(t,6-H, -CH_3 $J_{H\text{-}H} = 7.0$ Hz);IR: (neat) (KBr) υ(max): 2977, 2940, 2896 (C—H str), 1382(C—H bend), 1265(P═O), 1174(P-N-C), 1090, 1050(P-O-C) cm^{-1}. MS (EI): m/z (%) = 265(3), 250(78), 208 (45),166 (47), 124(100), 180 (4) 138 (20).

Dipropyl-N-ethyl-N-methylphosphoramidate

Bp: 109–110°C (1 mmHg); ^{31}P NMR (161.98 MHz, $CDCl_3$): $\delta = 10.37$. ^{1}H-NMR ($CDCl_3$): $\delta = 4.05$(m,4-H, -OCH_2, $J_{H\text{-}H} = 7.0$ $J_{H-P} = 8.0$ Hz), 3.25(m,2H,-CH_2-), 2.75(d,3H,CH_3), 1.74(m, 4H, CH_2),1.5(t,3H,CH_3), 0.97(t,6-H, -CH_3 $J_{H\text{-}H} = 7.0$ Hz).IR: (neat) (KBr) υ(max): 2970, 2945, (C—H str), 1378(C—H bend.), 1265(P═O), 1174(P-N-C), 1090, 1050(P-O-C) cm^{-1}. MS (EI): m/z (%) = 233(4), 208(39), 166 (31), 124(100), 138 (11), 110 (9), 106 (7), 58 (35).

Dipropyl-N-ethyl-N-propylphosphoramidate

Bp: 1127–1128°C (1 mmHg); ^{31}P NMR (161.98 MHz, $CDCl_3$): $\delta =$ 11.14. ^{1}H-NMR ($CDCl_3$): $\delta = 4.05$(m,4-H, -OCH_2, $J_{H\text{-}H} = 7.0$ $J_{H-P} =$ 8.0 Hz), 3.25(m,4H,-CH_2-N-), 1.74(m, 4H, CH_2),1.55 (m,2H,-CH_2-),1.15(t,3H,CH_3-), 0.97(t,6-H, -CH_3 $J_{H\text{-}H}$ =7.0 Hz), 0.88(t,3H, CH_3-).IR: (neat) (KBr) υ(max): 2977, 2950, (C—H Str), 1387(C—H bend), 1262(P═O),1160(P-N-C), 1090, 1050(P-O-C)cm^{-1}.MS (EI): m/z (%) = 251(2), 220(69), 180 (35), 138(100), 110 (24) 86(11).

Dipropyl-N-ethyl-N-isopropylphosphoramidate

Bp: 109–110°C (7 mmHg); ^{31}P NMR (161.98 MHz, $CDCl_3$): $\delta = 8.76$. ^{1}H-NMR ($CDCl_3$): $\delta = 4.05$(m, 4-H, -OCH_2, $J_{H\text{-}H} = 7.0$ J_{H-P} =8.0 Hz), 3.62(m,1H,-CH-), 3.20(m,2H,-CH_2-), 1.74(m, 4H,CH_2), 1.2(d,6H,CH_3-), 1.25(t,3H,CH_3), 0.97(t,6-H, -CH_3 $J_{H\text{-}H} = 7.0$ Hz).IR: (neat) (KBr) υ(max): 2975, 2947, (C—H stn), 1380 (C—H bend),1267 (P═O), 1167 (PNC), 1090,1050(P-O-C) cm^{-1}. MS (EI): m/z (%) = 251(2), 236(50), 194(18), 152(100), 124(23). 110 (21) 86(10).

Dipropyl-N-methyl-N-propylphosphoramidate

Bp: 97–98°C (2 mmHg); ^{31}P NMR (161.98 MHz, $CDCl_3$): $\delta = 11.12$.^{1}H-NMR ($CDCl_3$): $\delta = 4.05$(m,4-H, -OCH_2, $J_{H\text{-}H} = 7.0$ $J_{H-P} = 8.0$ Hz), 3.1(m,2H,-CH_2-N), 2.75 (d,3H,CH_3-N) 1.74(m, 4H, -CH_2),1.55(m,2H,-CH_2-), 0.97(t,6-H, -CH_3 $J_{H\text{-}H} = 7.0$ Hz), 0.89(t,3H, -CH_3). IR: (neat) (KBr) υ(max): 2976, 2953 (C—H str.), 1375(C—H bend), 1382(C—H bend),

1265(P=O),1174(P-N-C), 1085, 1045(P-O-C) cm^{-1}. MS (EI): m/z (%) = 237 (4), 208(61), 166 (39), 124(100), 110 (4) 152(9), 72(13).

Dipropyl-N-propyl-N-isopropylphosphoramidate

Bp:118–119°C (1 mmHg); ^{31}P NMR (161.98 MHz, $CDCl_3$): $\delta = 8.77$. ^1H-NMR ($CDCl_3$): $\delta = 4.05$(m,4-H, -OCH_2, $J_{H\text{-}H} = 7.0$ $J_{H-P} = 8.0$ Hz), 3.6(m,1H,-CH-), 3.1(m,2H,CH_2-N-), 1.74(m,4H,CH_2), 1.6(m,2H,-CH_2-), 1.2(d, 6H, CH_3), 0.97(t,6-H, -CH_3 $J_{H\text{-}H}$ =7.0 Hz), 0.88(t,3H,CH_3-).IR: (neat) (KBr) υ(max): 2976, 2953 (C—H str.), 1375(C—H bend), 1266(P=O),1165(P-N-C),1090, 1050(P-O-C) cm^{-1}.MS (EI): m/z (%) = 265(6), 250(33), 236(100), 208 (16), 194(33), 166 (47), 152(50), 110(81), 124 (24), 110 (10).

Dipropyl-N-methyl-N-isopropylphosphoramidate

Bp: 104–105°C (1 mmHg); ^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 10.97. ^1H-NMR ($CDCl_3$): $\delta = 4.05$(m,4-H, -OCH_2, $J_{H\text{-}H} = 7.0$ J_{H-P} = 8.0 Hz), 3.75(m, 1H, -CH-), 2.65(d,3H,CH_3-N-), 1.74(m, 4H, CH_2), 1.15 (d, 6H, CH_3), 0.97(t,6-H, -CH_3 $J_{H\text{-}H}$ =7.0 Hz).IR: (neat) (KBr) υ(max): 2980, 2955, (C—H str), 1372(C—H-bend), 1265(P=O), 1168 (P-NC), 1090,1050(P-O-C) cm^{-1}.MS (EI): m/z (%) = 237(2), 222(31), 180 (19), 138(100), 124 (40) 120(13), 72(10).

Diisopropyl-N,N-dimethylphosphoramidate

Bp: 92°C (1 mmHg); ^{31}P NMR (161.98 MHz, $CDCl_3$):δ = 9.33.^1H-NMR ($CDCl_3$):$\delta = 4.55$(sept,2-H,-OCH-, $J_{H\text{-}H} = 6.0$, $J_{H-P} = 6.0$, Hz), 2.9(d,6H, -NCH_3), 1.25(d,12-H, -CH_3 $J_{H\text{-}H} = 6.0$ Hz); IR: (neat) (KBr) υ(max): 2972, 2899, (C—H Str.), 1380, (C—H bend), 1262(P=O), 1160(P-N-C), 1090, 1050(P-O-C) cm^{-1}. MS (EI): m/z (%) = 209(3), 166 (7), 152(7), 150 (9), 126 (13), 124 (19), 108 (25), 44 (100)

Diisopropyl-N,N-diethylphosphoramidate

Bp: 115–116°C (1 mmHg); ^{31}P NMR (161.98 MHz, $CDCl_3$): $\delta = 8.17$. ^1H-NMR ($CDCl_3$): $\delta = 4.55$(sept,2-H, -OCH-, $J_{H\text{-}H} = 6.0$, J_{H-P} =6.0Hz), 3.3(m,4H,-CH_2-), 1.25(d,12-H, -CH_3 $J_{H\text{-}H} = 6.0$ Hz),1.2(t,6H,CH_3-). IR: (neat) (KBr) υ(max): 2943, 2989(C—H str.), 1385 C—H bend), 1268 (P=O), 1163 (P-NC), 1090,1050(P-O-C) cm^{-1}.

Diisopropyl-N,N-dipropylphosphoramidate

Bp: 107–108°C (1 mmHg); ^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 9.06.^1H-NMR ($CDCl_3$): $\delta = 4.55$(sept,2-H, -OCH-, $J_{H\text{-}H} = 6.0$, $J_{H-P} = 6.0$ Hz), 3.3(m,4H,-CH_2-N-), 1.75(m,4H, -CH_2-), 1.25(d,12-H, -CH_3, $J_{H\text{-}H}$ =6.0 Hz), 1.04 (t,6H,CH_3).IR: (neat) (KBr) υ(max): 2978,

2947, 2889 (C—H str.), 1365, (C—H bend.),1262(P═O), 1167(P-N-C), 1080,1040(P-O-C) cm^{-1}.

Diisopropyl-N,N-diisopropylphosphoramidate

Bp: 119–120°C (1 mmHg); ^{31}P NMR (161.98 MHz, $CDCl_3$): $\delta = 6.89$. ^1H-NMR ($CDCl_3$): $\delta = 4.55$(sept,2-H, -OCH-, $J_{H-H} = 6.0$, $J_{H-P} = 6.0$ Hz), 3.4(m,2H,-CH-N-), 1.4(d,12H,CH_3-),1.25(d,12-H, -CH_3, $J_{H-H} = 6.0$ Hz). IR: (neat) (KBr) υ(max): 2977, 2940, 2896 (C—H str), 1382(C—H bend), 1265(P═O), 1174(P-N-C), 1090, 1050(P-O-C) cm^{-1}. MS (EI): m/z (%) = 265(4), 250(32), 208(25), 180(7),166 (5), 138(100), 124(75).

Diisopropyl-N-ethyl-N-methylphosphoramidate

Bp: 104–105°C (1 mmHg); ^{31}P NMR (161.98 MHz, $CDCl_3$): $\delta = 8.27$.^1H-NMR ($CDCl_3$): $\delta = 4.55$(sept,2-H, -OCH-, $J_{H-H} = 6.0$, $J_{H-P} = 6.0$ Hz), 3.25(m,2H,-CH_2-), 2.75(d,3H,CH_3), 1.5(t,3H,CH_3), 1.25(d,12-H, -CH_3, $J_{H-H} = 6.0$ Hz).IR: (neat) (KBr) υ(max): 2970, 2945, (C—H str), 1378(C—H bend.), 1267(P═O), 1165(P-N-C), 1090, 1050(P-O-C) cm^{-1}.MS (EI): m/z (%) = 237(4), 222(11), 180(10), 152 (5), 138(100), 120(11).

Diisopropyl-N-ethyl-N-propylphosphoramidate

Bp: 125–126°C (1 mmHg); ^{31}P NMR (161.98 MHz, $CDCl_3$): $\delta = 9.04$.^1H-NMR ($CDCl_3$): $\delta = 4.55$(sept,2-H, -OCH-, $J_{H-H} = 6.0$, $J_{H-P} = 6.0$ Hz), 3.25(m,4H,-CH_2-N-), 1.55 (m,2H, -CH_2-), 1.15(t,3H,CH_3-), 1.25(d,12-H, CH_3-$J_{H-H} = 6.0$), 0.88(t,3H, CH_3-).IR: (neat) (KBr) υ(max): 2977, 2950, (C—H Str), 1387(C—H bend), 1272(P═O), 1160(P-N-C), 1088, 1047(P-O-C) cm^{-1}. MS (EI): m/z (%) = 251(3), 222(22), 180(22), 166 (7), 138(100), 110(20).

Diisopropyl-N-ethyl-N-isopropylphosphoramidate

Bp: 115–116°C (1.5 mmHg); ^{31}P NMR (161.98 MHz, $CDCl_3$): $\delta = 6.91$.^1H-NMR ($CDCl_3$): $\delta = 4.55$(sept,2-H, -OCH-, $J_{H-H} = 6.0$, $J_{H-P} = 6.0$ Hz), 3.9(m,1H,-CH-), 3.20(m,2H,-CH_2-), 1.23(t,3H,CH_3), 1.25(d,12-H, CH_3-, J_{H-H} =6.0 Hz), 1.2(d, 6H, CH3-).IR: (neat) (KBr) υ(max): 2975, 2947, (C—H str), 1380 (C—H bend), 1267 (P═O), 1167 (PNC), 1090, 1050(P-O-C) cm^{-1}.MS (EI): m/z (%) = 251(2), 236(19), 194(12), 152 (100), 138(100), 124(20), 110 (15).

Diisopropyl-N-methyl-N-propylphosphoramidate

Bp:112–113°C (1.5 mmHg); ^{31}P NMR (161.98 MHz, $CDCl_3$): $\delta = 9.02$.^1H-NMR ($CDCl_3$): $\delta = 4.55$(sept,2-H, -OCH-, $J_{H-H} = 6.0$, $J_{H-P} = 6.0$ Hz), 3.1(m,2H,-CH_2-N), 2.75(d,3H,CH_3-N) 1.55(m,2H,-CH_2-), 1.25(d,12-H, CH_3-$J_{H-H} = 6.0$ Hz),0.89(t,3H, CH_3-).IR: (neat) (KBr)

υ(max): 2976, 2953 (C—H str.), 1375(C—H bend), 1265(P═O), 1174(P-N-C), 1085, 1045(P-O-C) cm^{-1}. MS (EI): m/z (%) = 237(7), 208(46), 166 (17), 124(100), 152(9).

Diisopropyl-N-propyl-N-isopropylphosphoramidate

Bp: 116–117°C (1.2 mmHg); ^{31}P NMR (161.98 MHz, $CDCl_3$): $\delta = 6.88$. ^{1}H-NMR ($CDCl_3$): $\delta = 4.55$(sept,2-H, -OCH-, $J_{H\text{-}H} = 6.0$, $J_{H-P} = 6.0$ Hz), 3.6(m,1H,-CH-), 3.1(m,2H,CH_2-N-), 1.6(m,2H,-CH_2-), 1.2(d,6H,CH_3), 1.25(d,12-H, CH_3- $J_{H\text{-}H} = 6.0$ Hz),0.88(t,3H,CH_3-).IR: (neat) (KBr) υ(max): 2976, 2953 (C—H str.), 1375(C—H bend), 1270(P═O), 1165(P-N-C), 1090, 1050(P-O-C) cm^{-1}.MS (EI): m/z (%) = 265(4), 250(11), 236 (31), 180(4),166 (67), 124(17), 110(60).

Diisopropyl-N-methyl-N-isopropylphosphoramidate

Bp: 99–100°C (1 mmHg); ^{31}P NMR (161.98 MHz, $CDCl_3$): $\delta = 6.90$.^{1}H-NMR ($CDCl_3$): δ = 4.55(sept, 2-H, -OCH-, $J_{H\text{-}H} = 6.0$, $J_{H-P} = 6.0$ Hz), 3.75(m, 1H, -CH-N-),2.65(d,3H,CH_3-N-), 1.25 (d,12-H, CH_3-, $J_{H\text{-}H}$ = 6.0 Hz),1.15(d,6H,CH_3).IR: (neat) (KBr) υ (max): 2980, 2955,(C—H str), 1372(C—H-bend), 1265(P═O), 1168(P-N-C), 1090, 1050(P-O-C) cm^{-1}. MS (EI): m/z (%) = 237(3),222(11),180(10), 138(100), 124(35), 120(20).

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