

***N,N'*-Dichlorobis(2,4,6-trichlorophenyl)urea (CC-2): An Efficient Reagent for the Synthesis of Chemical Weapons Convention Related Dialkyl-*N,N'*-dialkylphosphoramidates from Dialkylphosphites**

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EXPERIMENTAL SECTION:

Materials: PCl_3 , symmetrical amines, alkanols and alumina were obtained from E. Merk (India). Diphenyl chlorophosphate, diphenylurea, unsymmetrical amines were purchased from Aldrich chemical company (USA). The propylisopropylamine and CC-2 were prepared by reported procedure²⁰. The purity of all the starting chemicals was checked before use. The solvents used were redistilled before use.

IR spectra were recorded on Bruker Tensor 27 FT-IR spectrometer on KBr disk. ¹H and ³¹P NMR spectra were recorded on Bruker DPX Avance 400 MHz FT- NMR in CDCl_3 using tetramethylsilane as an internal standard for ¹H and 85 % H_3PO_4 as an external standard for ³¹P NMR. 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 x 0.32 mm internal diameter x 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.

1. Dimethyl N,N-dimethylphosphoramidate:

Bp: 82-83 °C (6 mmHg); ³¹P NMR (161.98 MHz, CDCl₃): δ= 14.07.

¹H-NMR (400.13 MHz, CDCl₃): δ= 3.72(d, 6H, OCH₃ J_{H-P}=12.0Hz), 2.9(d, 6H, N-CH₃).

IR: Neat (KBr) ν(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).

2. Dimethyl N,N-diethylphosphoramidate:

Bp: 98-99 °C (5 mmHg); ³¹P NMR (161.98 MHz, CDCl₃): δ= 13.57.

¹H-NMR (CDCl₃): δ= 3.75(d, 6H, OCH₃ J_{H-P}=12.0Hz), 3.3(m,4H,-CH₂N-),

1.2(t,6H,CH₃-).

IR: (Neat) (KBr) ν(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).

3. Dimethyl N,N-dipropylphosphoramidate:

Bp: 92-93 °C (2 mmHg); ³¹P NMR (161.98 MHz, CDCl₃): δ= 13.81.

¹H-NMR (CDCl₃): δ = 3.78(d, 6H, OCH₃, J_{H-H}=12.0Hz), 3.3(m, 4H,-CH₂-N-), 1.75(m, 4H, -CH₂-), 1.0(t, 3H, CH₃).

IR: (neat) (KBr) ν(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) .

4. Dimethyl N,N-diisopropylphosphoramidate:

Bp: 95-96 °C (3 mmHg); ³¹P NMR (161.98 MHz, CDCl₃): δ= 11.51.

¹H-NMR (CDCl₃): δ = 3.80(d, 6-H, OCH₃ J_{H-H}=12.0Hz), 3.4(m, 2H,-CH-), 1.4(d, 12H, CH₃). IR (neat) (KBr) ν(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).

5. Dimethyl N-ethyl-N-methylphosphoramidate:

Bp: 83-85 °C (5 mmHg); ³¹P NMR (161.98 MHz, CDCl₃): δ= 13.87.

¹H-NMR (CDCl₃): δ = 3.78(d, 6-H, OCH₃ J_{H-H}=12.0Hz), 3.25(m,2H,-CH₂-), 2.75(d,3H, N-CH₃), 1.5(t,3H,CH₃).

IR: (neat) (KBr) ν(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).

6. Dimethyl N-ethyl-N-propylphosphoramidate:

Bp: 93-95 °C (3 mmHg); ³¹P NMR (161.98 MHz, CDCl₃): δ= 13.75.

¹H-NMR (CDCl₃): δ = 3.80(d, 6-H, OCH₃ J_{H-H}=12.0Hz), 3.25(m,4H,-CH₂-N-), 1.55 (m,2H,-CH₂-)1.15(t,3H,CH₃-), 0.88(t,3H, CH₃-).

IR: (neat) (KBr) ν(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).

7. Dimethyl N-ethyl-N-isopropylphosphoramidate:

Bp: 84-86 °C (4.5 mmHg); ³¹P NMR (161.98 MHz, CDCl₃): δ= 11.17.

$^1\text{H-NMR}$ (CDCl_3): $\delta = 3.79(\text{d}, 6\text{-H}, \text{OCH}_3, J_{\text{H-H}}=12.0\text{Hz})$, $3.9(\text{m}, 1\text{H}, \text{-CH-})$, $3.20(\text{m}, 2\text{H}, \text{-CH}_2\text{-})$, $1.25(\text{t}, 3\text{H}, \text{CH}_3)$, $1.2(\text{d}, 6\text{H}, \text{CH}_3\text{-})$.

IR: (neat) (KBr) $\nu(\text{max})$: 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)

8. Dimethyl N-methyl-N-propylphosphoramidate:

Bp: 98-99 $^{\circ}\text{C}$ (6 mmHg); ^{31}P NMR (161.98 MHz, CDCl_3): $\delta = 13.72$.

$^1\text{H-NMR}$ (CDCl_3): $\delta = 3.80(\text{d}, 6\text{-H}, \text{OCH}_3, J_{\text{H-H}}=12.0\text{Hz})$, $3.1(\text{m}, 2\text{H}, \text{-CH}_2\text{-N})$, $2.75(\text{d}, 3\text{H}, \text{CH}_3\text{-N})$, $1.55(\text{m}, 2\text{H}, \text{-CH}_2\text{-})$, $0.89(\text{t}, 3\text{H}, \text{CH}_3\text{-})$

IR: (neat) (KBr) $\nu(\text{max})$: 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).

9. Dimethyl N-propyl-N-isopropylphosphoramidate:

Bp: 98-99 $^{\circ}\text{C}$ (2 mmHg); ^{31}P NMR (161.98 MHz, CDCl_3): $\delta = 11.17$.

$^1\text{H-NMR}$ (CDCl_3): $\delta = 3.80(\text{d}, 6\text{-H}, \text{OCH}_3, J_{\text{H-H}}=12.0\text{Hz})$, $3.6(\text{m}, 1\text{H}, \text{-CH-})$, $3.21(\text{m}, 2\text{H}, \text{-CH}_2\text{-N-})$, $1.6(\text{m}, 2\text{H}, \text{-CH}_2\text{-})$, $1.2(\text{d}, 6\text{H}, \text{CH}_3\text{-})$, $0.88(\text{t}, 3\text{H}, \text{CH}_3\text{-})$.

IR: (neat) (KBr) $\nu(\text{max})$: 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).

10. Dimethyl N-methyl-N-isopropylphosphoramidate:

Bp: 88-89 $^{\circ}\text{C}$ (6 mmHg); ^{31}P NMR (161.98 MHz, CDCl_3): $\delta = 11.19$.

$^1\text{H-NMR}$ (CDCl_3): $\delta = 3.80(\text{d}, 6\text{-H}, \text{OCH}_3, J_{\text{H-H}}=12.0\text{Hz}), 3.75(\text{m}, 1\text{H}, \text{-CH-}), 2.73(\text{d}, 3\text{H}, \text{CH}_3\text{-N-}), 1.15(\text{d}, 6\text{H}, \text{CH}_3)$.

IR: (neat) (KBr) $\nu(\text{max})$: 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).

11. Diethyl N,N-dimethylphosphoramidate:

Bp: 82-83 $^{\circ}\text{C}$ (5 mmHg); ^{31}P NMR (161.98 MHz, CDCl_3): $\delta = 11.45$.

$^1\text{H-NMR}$ (CDCl_3): $\delta = 4.25(\text{m}, 4\text{-H}, \text{-OCH}_2, J_{\text{H-H}}=7.0, J_{\text{H-P}}=8.0 \text{ Hz}), 2.79(\text{d}, 6\text{H}, \text{N-CH}_3), 1.33(\text{t}, 6\text{-H}, \text{-CH}_3, J_{\text{H-H}}=7.0 \text{ Hz})$.

IR: (neat) (KBr) $\nu(\text{max})$: 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).

12. Diethyl N,N-diethylphosphoramidate:

Bp: 109-110 $^{\circ}\text{C}$ (1 mmHg); ^{31}P NMR (161.98 MHz, CDCl_3): $\delta = 10.87$.

$^1\text{H-NMR}$ (CDCl_3): $\delta = 4.25(\text{m}, 4\text{-H}, \text{-OCH}_2, J_{\text{H-H}}=7.0, J_{\text{H-P}}=8.0 \text{ Hz}), 3.3 (\text{m}, 4\text{H}, \text{-CH}_2\text{-}), 1.33 (\text{t}, 6\text{-H}, \text{CH}_3, J_{\text{H-H}}=7.0\text{Hz}), 1.2 (\text{t}, 6\text{H}, \text{CH}_3\text{-}),$

IR: (neat) (KBr) $\nu(\text{max})$: 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)

13. Diethyl N,N-dipropylphosphoramidate:

Bp: 110-111 $^{\circ}\text{C}$ (2 mmHg); ^{31}P NMR (161.98 MHz, CDCl_3): $\delta = 11.09$.

$^1\text{H-NMR}$ (CDCl_3) : $\delta = 4.25(\text{m}, 4\text{-H}, -\text{OCH}_2, J_{\text{H-H}}=7.0 J_{\text{H-P}}=8.0 \text{ Hz}), 3.3(\text{m}, 4\text{H}, -\text{CH}_2\text{-N-}), 1.75(\text{m}, 4\text{H}, -\text{CH}_2\text{-}), 1.33(\text{t}, 6\text{-H}, \text{CH}_3 J_{\text{H-H}}=7.0\text{Hz}), 1.0(\text{t}, 6\text{H}, \text{CH}_3), ;$

IR: (neat) (KBr) $\nu(\text{max})$: 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).

14. Diethyl N,N-diisopropylphosphoramidate:

Bp: 116-117 $^{\circ}\text{C}$ (1 mmHg); ^{31}P NMR (161.98 MHz, CDCl_3): $\delta = 8.80$.

$^1\text{H-NMR}$ (CDCl_3) : $\delta = 4.25(\text{m}, 4\text{-H}, -\text{OCH}_2, J_{\text{H-H}}=7.0 J_{\text{H-P}}=8.0 \text{ Hz}), 3.4(\text{m}, 2\text{H}, -\text{CH-}), 1.4(\text{d}, 12\text{H}, \text{CH}_3\text{-}), 1.31(\text{t}, 6\text{-H}, \text{CH}_3 J_{\text{H-H}}=7.0\text{Hz})$.

IR: (neat) (KBr) $\nu(\text{max})$: 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).

15. Diethyl N-ethyl-N-methylphosphoramidate:

Bp: 109-110 $^{\circ}\text{C}$ (1 mmHg); ^{31}P NMR (161.98 MHz, CDCl_3): $\delta = 10.77$.

$^1\text{H-NMR}$ (CDCl_3) : $\delta = 4.25(\text{m}, 4\text{-H}, -\text{OCH}_2, J_{\text{H-H}}=7.0 J_{\text{H-P}}=8.0 \text{ Hz}), 3.25(\text{m}, 2\text{H}, -\text{CH}_2\text{-}), 2.75(\text{d}, 3\text{H}, \text{CH}_3), 1.5(\text{t}, 3\text{H}, \text{CH}_3), 1.33(\text{t}, 6\text{-H}, \text{CH}_3 J_{\text{H-H}}=7.0\text{Hz})$.

IR: (neat) (KBr) $\nu(\text{max})$: 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)

16. Diethyl N-ethyl-N-propylphosphoramidate:

Bp: 121-122 $^{\circ}\text{C}$ (1 mmHg); ^{31}P NMR (161.98 MHz, CDCl_3): $\delta = 11.06$.

$^1\text{H-NMR}$ (CDCl_3) : $\delta = 4.25(\text{m}, 4\text{-H}, -\text{OCH}_2, J_{\text{H-H}}=7.0 J_{\text{H-P}}=8.0 \text{ Hz}), 3.26(\text{m}, 4\text{H}, -\text{CH}_2\text{-N-}), 1.54 (\text{m}, 2\text{H}, -\text{CH}_2\text{-}), 1.34(\text{t}, 6\text{-H}, -\text{CH}_3 J_{\text{H-H}}=7.0\text{Hz}), 1.14(\text{t}, 3\text{H}, \text{CH}_3\text{-}), 0.89(\text{t}, 3\text{H}, \text{CH}_3\text{-})$.

IR: (neat) (KBr) $\nu(\text{max})$: 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).

17. Diethyl N-ethyl-N-isopropylphosphoramidate:

Bp: 92-93 $^{\circ}\text{C}$ (10 mmHg); ^{31}P NMR (161.98 MHz, CDCl_3): δ = 8.66.

^1H -NMR (CDCl_3) : δ = 4.23(m, 4-H, $-\text{OCH}_2$, $J_{\text{H-H}}=7.0$ $J_{\text{H-P}}=8.0$ Hz), 3.91(m, 1H, $-\text{CH}-$), 3.21(m, 2H, $-\text{CH}_2-$), 1.33(t, 6-H, $-\text{CH}_3$ $J_{\text{H-H}}=7.0$ Hz), 1.21(d, 6H, CH_3-), 1.24(t, 3H, $-\text{CH}_3$)

IR: (neat) (KBr) $\nu(\text{max})$: 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 (%) = 233(4), 208(100), 180 (35), 152 (92), 166 (21), 152(90), 138 (12), 124 (25), 110 (21), 86 (11).

18. Diethyl N-methyl-N-propylphosphoramidate:

Bp: 81-82 $^{\circ}\text{C}$ (1 mmHg); ^{31}P NMR (161.98 MHz, CDCl_3): δ = 11.02.

^1H -NMR (CDCl_3) : δ = 4.25(m, 4-H, $-\text{OCH}_2$, $J_{\text{H-H}}=7.0$ $J_{\text{H-P}}=8.0$ Hz), 3.1(m, 2H, $-\text{CH}_2-\text{N}$), 2.75(d, 3H, CH_3-N) 1.55(m, 2H, $-\text{CH}_2-$), 1.33(t, 6-H, $-\text{CH}_3$ $J_{\text{H-H}}=7.0$ Hz), 0.89(t, 3H, $-\text{CH}_3$).

IR: (neat) (KBr) $\nu(\text{max})$: 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).

19. Diethyl N-propyl-N-isopropylphosphoramidate:

Bp: 95-96 $^{\circ}\text{C}$ (1 mmHg); ^{31}P NMR (161.98 MHz, CDCl_3): δ = 11.57.

$^1\text{H-NMR}$ (CDCl_3): $\delta = 4.25(\text{m}, 4\text{-H}, -\text{OCH}_2, J_{\text{H-H}}=7.0 J_{\text{H-P}}=8.0 \text{ Hz}), 3.6(\text{m}, 1\text{H}, -\text{CH-}), 3.1(\text{m}, 2\text{H}, \text{CH}_2\text{-N-}), 1.6(\text{m}, 2\text{H}, -\text{CH}_2\text{-}), 1.33(\text{t}, 6\text{-H}, -\text{CH}_3 J_{\text{H-H}}=7.0\text{Hz}), 1.2(\text{d}, 6\text{H}, \text{CH}_3\text{-}), 0.88(\text{t}, 3\text{H}, \text{CH}_3\text{-})$

IR: (neat) (KBr) $\nu(\text{max})$: 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).

20. Diethyl N-methyl-N-isopropylphosphoramidate:

Bp: 98-990 $^{\circ}\text{C}$ (0.5 mmHg); ^{31}P NMR (161.98 MHz, CDCl_3): $\delta = 10.77$.

$^1\text{H-NMR}$ (CDCl_3): $\delta = 4.25(\text{m}, 4\text{-H}, -\text{OCH}_2, J_{\text{H-H}}=7.0 J_{\text{H-P}}=8.0 \text{ Hz}), 3.75(\text{m}, 1\text{H}, -\text{CH-}), 2.65(\text{d}, 3\text{H}, \text{CH}_3\text{-N-}), 1.33(\text{t}, 6\text{-H}, -\text{CH}_3 J_{\text{H-H}}=7.0\text{Hz}), 1.15(\text{d}, 6\text{H}, \text{CH}_3)$.

IR: (neat) (KBr) $\nu(\text{max})$: 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).

21. Diproyl N,N-dimethylphosphoramidate:

Bp: 92-93 $^{\circ}\text{C}$ (3 mmHg); ^{31}P NMR (161.98 MHz, CDCl_3): $\delta = 11.51$.

$^1\text{H-NMR}$ (CDCl_3): $\delta = 4.05(\text{m}, 4\text{-H}, -\text{OCH}_2, J_{\text{H-H}}=7.0 J_{\text{H-P}}=8.0 \text{ Hz}), 2.9(\text{d}, 6\text{H}, -\text{NCH}_3), 1.74(\text{m}, 4\text{H}, -\text{CH}_2), 0.97(\text{t}, 6\text{-H}, -\text{CH}_3 J_{\text{H-H}}=7.0\text{Hz});$

IR: (neat) (KBr) $\nu(\text{max})$: 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)

22. Diproyl N,N-diethylphosphoramidate:

Bp: 119-120 °C (1 mmHg); ³¹P NMR (161.98 MHz, CDCl₃): δ= 10.27.

¹H-NMR (CDCl₃): δ = 4.05(m,4-H, -OCH₂, J_{H-H}=7.0 J_{H-P}=8.0 Hz), 3.3(m,4H,-CH₂-), 1.74(m, 4H, CH₂), 1.2(t,6H,CH₃-), 0.97(t,6-H, -CH₃ J_{H-H}=7.0Hz);

IR: (neat) (KBr) ν(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).

23. Dipropyl N,N-dipropylphosphoramidate:

Bp: 113-114 °C (1 mmHg); ³¹P NMR (161.98 MHz, CDCl₃): δ= 11.22.

¹H-NMR (CDCl₃): δ = 4.05(m,4-H, -OCH₂, J_{H-H}=7.0 J_{H-P}=8.0 Hz), 3.3(m,4H,-CH₂-N-), 1.72- 1.76 (m, 8H, -CH₂-), 1.02(t,3H,CH₃), 0.97(t,6-H, -CH₃ J_{H-H}=7.0Hz);

IR: (neat) (KBr) ν(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).

24. Dipropyl N,N-diisopropylphosphoramidate:

Bp: 123-124 °C (1 mmHg); ³¹P NMR (161.98 MHz, CDCl₃): δ= 8.90.

¹H-NMR (CDCl₃): δ = 4.05(m,4-H, -OCH₂, J_{H-H}=7.0 J_{H-P}=8.0 Hz), 3.4(m,2H,-CH-), 1.74(m, 4H, CH₂), 1.4(d,12H,CH₃-), 0.97(t,6-H, -CH₃ J_{H-H}=7.0Hz);

IR: (neat) (KBr) ν(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).

25. Dipropyl N-ethyl-N-methylphosphoramidate:

Bp: 109-110 °C (1 mmHg); ³¹P NMR (161.98 MHz, CDCl₃): δ= 10.37.

¹H-NMR (CDCl₃) : δ = 4.05(m,4-H, -OCH₂, J_{H-H}=7.0 J_{H-P}=8.0 Hz), 3.25(m,2H,-CH₂-), 2.75(d,3H,CH₃), 1.74(m, 4H, CH₂),1.5(t,3H,CH₃), 0.97(t,6-H, -CH₃ J_{H-H}=7.0 Hz).

IR: (neat) (KBr) ν(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).

26. Dipropyl N-ethyl-N-propylphosphoramidate:

Bp: 1127-1128 °C (1 mmHg); ³¹P NMR (161.98 MHz, CDCl₃): δ= 11.14.

¹H-NMR (CDCl₃) : δ = 4.05(m,4-H, -OCH₂, J_{H-H}=7.0 J_{H-P}=8.0 Hz), 3.25(m,4H,-CH₂-N-), 1.74

(m, 4H, CH₂),1.55 (m,2H,-CH₂-), 1.15 (t,3H,CH₃-), 0.97 (t,6-H, -CH₃ J_{H-H}=7.0 Hz), 0.88(t,3H, CH₃-).

IR: (neat) (KBr) ν(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).

27. Dipropyl N-ethyl-N-isopropylphosphoramidate:

Bp: 109-110 °C (7 mmHg); ³¹P NMR (161.98 MHz, CDCl₃): δ= 8.76.

¹H-NMR (CDCl₃) : δ = 4.05(m,4-H, -OCH₂, J_{H-H}=7.0 J_{H-P}=8.0 Hz),3.62(m,1H,-CH-), 3.20(m,2H,-CH₂-),1.74(m, 4H, CH₂),1.2(d,6H,CH₃-), 1.25(t,3H,CH₃), 0.97(t,6-H, -CH₃ J_{H-H}=7.0 Hz).

IR: (neat) (KBr) ν(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(50), 194(18), 152(100), 124(23). 110 (21) 86(10).

28. Dipropyl N-methyl-N-propylphosphoramidate:

Bp: 97-98 °C (2 mmHg); ³¹P NMR (161.98 MHz, CDCl₃): δ= 11.12.

¹H-NMR (CDCl₃) : δ = 4.05(m,4-H, -OCH₂, J_{H-H}=7.0 J_{H-P}=8.0 Hz), 3.1(m,2H,-CH₂-N), 2.75(d,3H,CH₃-N) 1.74(m, 4H, -CH₂),1.55(m,2H,-CH₂-), 0.97(t,6-H, -CH₃ J_{H-H}=7.0 Hz), 0.89(t,3H, -CH₃).

IR: (neat) (KBr) ν(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).

29. Dipropyl N-propyl-N-isopropylphosphoramidate:

Bp: 118-119 °C (1 mmHg); ³¹P NMR (161.98 MHz, CDCl₃): δ= 8.77.

¹H-NMR (CDCl₃) : δ = 4.05(m,4-H, -OCH₂, J_{H-H}=7.0 J_{H-P}=8.0 Hz), 3.6(m,1H,-CH-), 3.1(m,2H,CH₂-N-), 1.74(m, 4H, CH₂),1.6(m,2H,-CH₂-), 1.2(d,6H,CH₃), 0.97(t,6-H, -CH₃ J_{H-H}=7.0 Hz), 0.88(t,3H,CH₃-).

IR: (neat) (KBr) ν(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).

30. Dipropyl N-methyl-N-isopropylphosphoramidate:

Bp: 104-105 °C (1 mmHg); ³¹P NMR (161.98 MHz, CDCl₃): δ= 10.97.

¹H-NMR (CDCl₃) : δ = 4.05(m,4-H, -OCH₂, J_{H-H}=7.0 J_{H-P}=8.0 Hz), 3.75(m, 1H, -CH-), 2.65(d,3H,CH₃-N-), 1.74(m, 4H, CH₂), 1.15(d,6H,CH₃), 0.97(t,6-H, -CH₃ J_{H-H}=7.0 Hz).

IR: (neat) (KBr) $\nu(\text{max})$: 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).

31. Diisopropyl N,N-dimethylphosphoramidate:

Bp: 92 $^{\circ}\text{C}$ (1 mmHg); ^{31}P NMR (161.98 MHz, CDCl_3): δ = 9.33.

^1H -NMR (CDCl_3) : δ = 4.55(sept,2-H, -OCH-, $J_{\text{H-H}}=6.0$, $J_{\text{H-P}}=6.0$, Hz), 2.9(d,6H, -NCH₃), 1.25(d,12-H, -CH₃ $J_{\text{H-H}}=6.0$ Hz);

IR: (neat) (KBr) $\nu(\text{max})$: 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)

32. Diisopropyl N,N-diethylphosphoramidate:

Bp: 115-116 $^{\circ}\text{C}$ (1 mmHg); ^{31}P NMR (161.98 MHz, CDCl_3): δ = 8.17.

^1H -NMR (CDCl_3) : δ = 4.54(sept,2-H, -OCH-, $J_{\text{H-H}}=6.0$, $J_{\text{H-P}}=6.0\text{Hz}$), 3.30(m,4H,-CH₂-), 1.25(d,12-H, -CH₃ $J_{\text{H-H}}=6.0$ Hz),1.20(t,6H,CH₃-).

IR: (neat) (KBr) $\nu(\text{max})$: 2943, 2989(C-H str.), 1385 C-H bend), 1268 (P=O), 1163 (P-NC), 1090,1050(P-O-C) cm^{-1} .

33. Diisopropyl N,N-dipropylphosphoramidate:

Bp: 107-108 $^{\circ}\text{C}$ (1 mmHg); ^{31}P NMR (161.98 MHz, CDCl_3): δ = 9.06.

^1H -NMR (CDCl_3) : δ = 4.56(sept,2-H, -OCH-, $J_{\text{H-H}}=6.0$, $J_{\text{H-P}}=6.0$ Hz), 3.30(m,4H,-CH₂-N-), 1.75(m,4H, -CH₂-), 1.25(d,12-H, -CH₃, $J_{\text{H-H}}=6.0$ Hz), 1.04(t,6H,CH₃).

IR: (neat) (KBr) $\nu(\text{max})$: 2978, 2947, 2889 (C-H str.), 1365, (C-H bend.), 1262(P=O), 1167(P-N-C), 1080, 1040(P-O-C) cm^{-1} .

34. Diisopropyl N,N-diisopropylphosphoramidate:

Bp: 119-120 $^{\circ}\text{C}$ (1 mmHg); ^{31}P NMR (161.98 MHz, CDCl_3): δ = 6.89.

^1H -NMR (CDCl_3) : δ = 4.55(sept, 2-H, -OCH-, $J_{\text{H-H}}=6.0$, $J_{\text{H-P}}=6.0$ Hz), 3.4(m, 2H, -CH-N-), 1.4(d, 12H, CH_3 -), 1.25(d, 12-H, - CH_3 , $J_{\text{H-H}}=6.0$ Hz).

IR: (neat) (KBr) $\nu(\text{max})$: 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).

35. Diisopropyl N-ethyl-N-methylphosphoramidate:

Bp: 104-105 $^{\circ}\text{C}$ (1 mmHg); ^{31}P NMR (161.98 MHz, CDCl_3): δ = 8.27.

^1H -NMR (CDCl_3) : δ = 4.55(sept, 2-H, -OCH-, $J_{\text{H-H}}=6.0$, $J_{\text{H-P}}=6.0$ 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 , $J_{\text{H-H}}=6.0$ Hz).

IR: (neat) (KBr) $\nu(\text{max})$: 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).

36. Diisopropyl N-ethyl-N-propylphosphoramidate:

Bp: 125-126 $^{\circ}\text{C}$ (1 mmHg); ^{31}P NMR (161.98 MHz, CDCl_3): δ = 9.04.

^1H -NMR (CDCl_3) : δ = 4.55(sept, 2-H, -OCH-, $J_{\text{H-H}}=6.0$, $J_{\text{H-P}}=6.0$ 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 - $J_{\text{H-H}}=6.0$), 0.88(t, 3H, CH_3 -)

IR: (neat) (KBr) $\nu(\text{max})$: 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).

37. Diisopropyl N-ethyl-N-isopropylphosphoramidate:

Bp: 115-116 °C (1.5 mmHg); ³¹P NMR (161.98 MHz, CDCl₃): δ= 6.91.

¹H-NMR (CDCl₃) : δ= 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,-CH₂-),1.23(t,3H,CH₃), 1.25(d,12-H, CH₃-, J_{H-H}=6.0 Hz), 1.2(d, 6H, CH₃-).

IR: (neat) (KBr) ν(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).

38. Diisopropyl N-methyl-N-propylphosphoramidate:

Bp:112-113 °C (1.5 mmHg); ³¹P NMR (161.98 MHz, CDCl₃): δ= 9.02.

¹H-NMR (CDCl₃) : δ = 4.55(sept,2-H, -OCH-, J_{H-H}=6.0, J_{H-P}=6.0 Hz), 3.1(m,2H,-CH₂-N), 2.75(d,3H,CH₃-N) 1.55(m,2H,-CH₂-), 1.25(d,12-H, CH₃-J_{H-H}=6.0 Hz),0.89(t,3H, CH₃-).

IR: (neat) (KBr) ν(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).

39. Diisopropyl N-propyl-N-isopropylphosphoramidate:

Bp: 116-117 °C (1.2 mmHg); ³¹P NMR (161.98 MHz, CDCl₃): δ= 6.88.

¹H-NMR (CDCl₃) : δ = 4.55(sept,2-H, -OCH-, J_{H-H}=6.0, J_{H-P}=6.0 Hz), 3.6(m,1H,-CH-), 3.1(m,2H,CH₂-N-), 1.6(m,2H,-CH₂-), 1.2(d,6H,CH₃), 1.25(d,12-H, CH₃- J_{H-H}=6.0 Hz),0.88(t,3H,CH₃-).

IR: (neat) (KBr) $\nu(\text{max})$: 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).

40. Diisopropyl N-methyl-N-isopropylphosphoramidate:

Bp: 99-100 $^{\circ}\text{C}$ (1 mmHg); ^{31}P NMR (161.98 MHz, CDCl_3): δ = 6.90.

^1H -NMR (CDCl_3): δ = 4.56(sept, 2-H, -OCH-, $J_{\text{H-H}}=6.0$, $J_{\text{H-P}}=6.0$ Hz), 3.75(m, 1H, -CH-N-), 2.65(d,3H, CH_3 , -N-), 1.25(d,12-H, CH_3 -, $J_{\text{H-H}}=6.0$ Hz),1.15(d,6H, CH_3).

IR: (neat) (KBr) $\nu(\text{max})$: 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).