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Synthesis of Block Copolymers Modified with Phosphonate Ester Groups Using Nitroxide-Mediated Radical Polymerization

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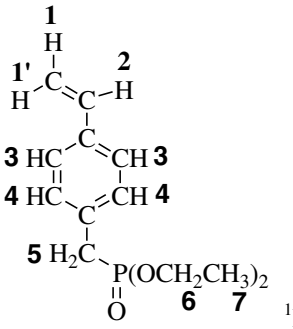
Experimental Part

Synthesis of diethyl-4-vinyl benzyl phosphonate (DEVBP)

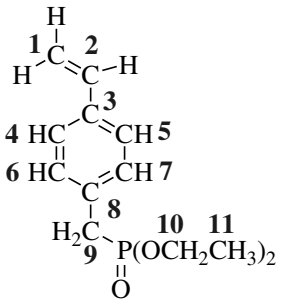
$C_{13}H_{19}PO_3$

M_r = 254.27 g/mol

Storage at - 22 °C



^{1}H-NMR



^{13}C-NMR

TLC: *n*-hexane/ethyl acetate 2:1, UV, R_f = 0.04.

IR (KBr) : ν (cm^{-1}) = 3086 (w, C=CH_2 (C-H-valence)), 2983-2908 (s, CH_2, CH_3 (C-H-valence)), 2870 (w, CH), 1630 (m, C=C), 1610, 1512 (w, m, aromatic. C=C), 1443 (CH_2, CH_3

(C-H-deformation)), 1408-1392 (m, P-O-alkyl), 1249 (s, P=O), 1055-1026 (s, P-O-alkyl), 988, 910 (m, R-CH=CH_2 (C-H)), 857 (s, 1,4-disubst. aromatic ring (C-H)-δ (out of plane)).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.32 (m, 2H-4), 7.23 (m, 2H-3), 6.66 (m, 1H-2), 5.70 (d, 1H-1', $J_{1',2}$ = 17.6 Hz), 5.20 (d, 1H-1, $J_{1,2}$ = 10.9 Hz), 3.99 (m, 4H-6), 3.11 (d, 2H-5, $J_{5,4}$ = 21.7 Hz), 1.22 (t, 6H-7, $J_{7,6}$ = 25.1 Hz).

^{13}C NMR (500 MHz, $CDCl_3$): δ (ppm) = 136.33 (CH-2), 136.12 (C-3), 131.07 (C-8), 129.85 (aromat. C-6,7[7]) , 129.80 (aromat. C-6,7), 126.29 (aromat. C-4,5), 126.26 (aromat. C-4,5), 113.60 (CH_2-1), 62.05 (CH_2-10), 33.99 (CH_2-9), 32.90 (CH_2-9), 16.29 (CH_3-11).

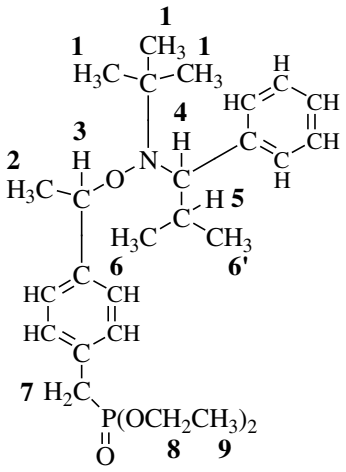
($C_{13}H_{19}PO_3$) (254.27 g/mol): Calcd. C 61.40, H 7.55; Found C 62.56, H 7.63.

*Synthesis of 2,2,5-trimethyl-3-(1'-p-methylen diethyl phosphonate phenylethoxy)-4-phenyl-3-azahexane (*DEVBP*TIPNO)*

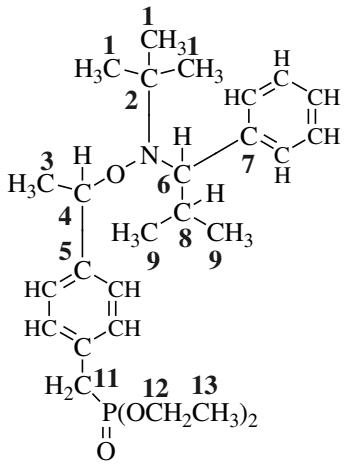
$C_{27}H_{42}PO_4N$

M_r = 475.63 g/mol

Storage at - 22 °C



^{1}H-NMR



^{13}C-NMR

TLC: ethyl acetate, UV, R_f = 0.36.

IR (KBr): ν (cm^{-1}) = 2974-2907 (s, CH_2, CH_3 (C-H-valence)), 2868 (m, CH), 1603, 1513 (w, m, aromatic. C=C), 1453 (m, CH_2, CH_3 (C-H-deformation)), 1390-1370 (m, P-O-alkyl), 1249 (s, P=O), 1056-1029 (s, P-O-alkyl), 839 (m, 1,4-disubst. aromatic ring (C-H)-δ (out of plane)).

^{1}H NMR (500 MHz, $CDCl_3$, both diastereomers): δ (ppm) = 7.38-7.14 (m, x H, phenyl), 4.87-4.84 (m, 2H-3a,3b), 4.00-3.89 (m, 8H-8), 3.37 (d, 1H-4b, $J_{4,5}$ = 10.6 Hz), 3.25 (d, 1H-4a, $J_{4,5}$ = 10.8 Hz), 3.18-3.10 (m, 4H-7), 2.29 (m, 1H-5b), 1.58 (d, 3H-2b, $J_{2,1}$ = 6.6 Hz), 1.49 (d, 3H-2a, $J_{2,1}$ = 6.6 Hz), 1.30 (m, 1H-5a), 1.27 (d, 3H-6b, $J_{6,8}$ = 6.3 Hz), 1.22-1.15 (m, 12H-9), 1.00 (s, 9H-1a), 0.88 (d, 3H-6a, $J_{6,8}$ = 6.3 Hz), 0.71 (s, 9H-1b), 0.51 (d, 3H-6'a, $J_{6,8}$ = 6.6 Hz), 0.20 (d, 3H-6'a, $J_{6,8}$ = 6.6 Hz).

^{13}C NMR (500 MHz, $CDCl_3$, both diastereomers): δ (ppm) = 144.45 (C-7), 143.70 (C-10), 142.31 (C-5), 130.87 (aromat.C), 129.89 (aromat.C), 129.48 (aromat.C), 127.34 (aromat.C), 127.14 (aromat.C), 126.40 (aromat.C), 126.34 (aromat. C), 126.30 (aromat.C), 126.13 (aromat.C), 83.22 (CH-4), 82.54 (CH-4), 72.18 (CH-6), 72.04 (CH-6), 62.09 (CH2-12), 60.46 (C-2), 60.26 (C-2), 34.04 (CH_2-11), 32.94 (CH_2-11), 31.97 (CH-8), 31.59 (CH-8), 28.35 (CH_3-1), 28.18 (CH_3-1), 24.59 (CH_3-3), 23.21 (CH_3-3), 22.05 (CH_3-9), 21.92 (CH_3-9), 21.12 (CH_3-9), 21.00 (CH_3-9), 16.33 (CH_3-12).

($C_{27}H_{42}PO_4N$) (475.63 g/mol): Calcd. C 68.18, H 8.91, N 2.95; Found C 68.16, H 8.00, N 2.82.

Hydrolysis of PDEVBP

^{31}P-NMR (120 MHz, $CDCl_3$/CD_3OD): δ (ppm) = 26.7 (before hydrolysis), 23.1 (after hydrolysis)