Synthesis of diethyl oxo phosphonates from monoterpene ketones – carvone, pinocarvone and 2-caren-4-one

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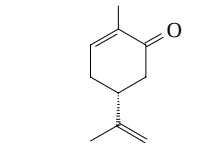
Reaction of α,β-unsaturated monoterpenic ketones – carvone, pinocarvone and 2-caren-4-one – with the sodium salt of diethylphosphite in diethylphosphite media results in regioselective addition to the conjugated carbon–carbon double bond and formation of the corresponding oxophosphonates.

Utilization of available natural terpenic compounds in the syntheses of novel biologically active compounds and chiral auxiliaries requires selective methods for the introduction of heteroatomic functional groups that significantly change the polarity, solubility and coordination ability of the terpenic molecules. Different phosphorus-containing groups are among the most interesting ones. Many organophosphorus compounds possess biological activity. The search for new biologically active phosphorus-containing molecules is being intensively carried out,[1–3] especially in the series of optically active compounds with chiral phosphorus[4,5] and those possessing chirality at the neighbouring carbons.[4–6] The use of chiral organophosphorus compounds in enantioselective catalysis is also well-documented, a few examples of phosphorylated terpenes showing them to be promising chiral auxiliaries.[7,8] Among the phosphorus-containing derivatives of terpenes, only monophosphates and pyrophosphates of allyl-type acyclic alcohols (geraniol, nerol, linalool, farnesol, nerolidol, *etc.*) have been intensively studied because of their importance in the biosynthesis of terpenoids in plants. Due to the lability of terpenes and the rather drastic conditions required for preparation of phosphorus-derivatives from unsaturated compounds, there are no general selective methods for introducing phosphorus into the terpene molecules, although organophosphorus compounds derived from natural terpenes might be of great interest from many points of view. We wish to report now the results of our study on the regioselective phosphorylation of certain terpenes by addition of diethyl-phosphite to α,β-unsaturated monoterpenic ketones – carvone **1**, pinocarvone **2** and 2-caren-4-one **3** – which are the simplest oxygenated derivatives of the widespread natural terpenes limonene, pinene and carene to be available in optically active form on an industrial scale.



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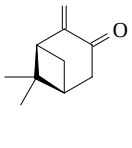

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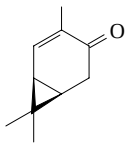

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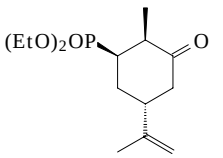
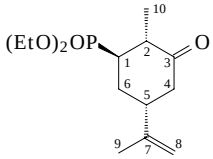


4a



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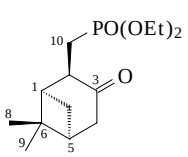

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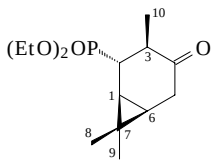

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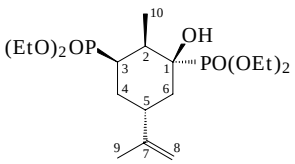

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Carvone was purchased from Fluka ($[\alpha]_{546}$ –73.5). Pinocarvone was prepared by photooxidation of α-pinene,[9] isolated from the turpentine of *Pinus silvestris L.*, in the presence of tetraphenylporphine.[10] 2-Caren-4-one was synthesized from (+)-3-carene (which was also isolated from the same turpentine) by nitrosochlorination–dehydrochlorination followed by hydrolytic deoximation.[11,12]

As found for the simplest compounds such as mesityl oxide and 1-acetylcyclohexene,[13,14] addition of dialkyl esters of phosphorus(III) acids to α,β-unsaturated carbonyl compounds takes place when alkoxides of alkali metals are used as catalysts. The use of trimethylsilyldiethylphosphite as a phosphorus-containing component is also known.[15] In this case, solvent and reaction temperature affect significantly the regioselectivity of the addition. In addition, the reaction occurs at temperatures about 180 °C, but this is impossible for selective addition to terpenic compounds because such a high temperature usually results in isomerization or destruction of the terpenic molecules. Another attempt at using silicon-containing phosphorus derivatives led to the synthesis of phosphinic acids from hypophosphites,[16] but this reaction was also studied in the case of very simple compounds such as esters of acrylic, benzylacrylic and crotonic acids.

Standard procedures for addition of diethylphosphite to unsaturated carbonyl compounds[13,14] were found to be unusable in the case of the terpenic ketones because of the low yields of the desired products. We have developed the following procedure leading to regioselective addition of diethylphosphite to conjugated carbon–carbon double bonds and formation of oxophosphonates in good yields. Sodium (0.07 g, 3.04 mmol) was added portionwise at room temperature to diethylphosphite (5 ml) followed by addition of unsaturated terpenic ketone (0.5 g, 3.33 mmol) to the resulting solution. After a certain period of time the reaction mixture was diluted with water (100 ml) and extracted with EtOAc (80 ml). The organic extract was washed with 30% aq. NaOH (3×50 ml), water (50 ml), brine and dried over anhydrous Na_2SO_4. Removal of the solvent under reduced pressure leaves a crude product containing the desired product and only a small amount of impurities (NMR). Analytical samples were obtained by liquid chromatography (Bruker LC-21 instrument, column: 125×4.6 mm packed with Nucleosil C18, eluent MeOH–H_2O = 1:3). The reaction of carvone **1** was performed for 3 h at –10 to –15 °C, pinocarvone **2** for 30 min at room temperature, and carenone **3** at 100–120 °C for 10 min.

The reaction of ketones **1**–**3** resulted in the stereoselective formation of oxophosphonates, the primary reaction products being transformed to equilibrium mixtures of epimers on prolonged reaction time. Although the primary reaction product **5**† seems to be less stable than its C-2 epimer (molecular mechanics, semi-empirical calculations), compound **5** is quite stable and is not transformed to the epimer. The product from

carvone is the least stable to isomerization: the primary isomer **4a** at room temperature without any catalyst is transformed to an equilibrium mixture of **4a** and **4b** (*ca.* 1:3).‡ In the case of carane derivative **3**, increase in the reaction time or prolonged storage at room temperature of the initially formed compound **6** leads to a *ca.* 3:1 mixture of **6**§ and its C-3 epimer.

† (±)-(1*S**,2*R**,5*S**)-6,6-*Dimethyl*-3-*oxobicyclo*[3.1.1]*hept*-2-*ylmethyl*-*phosphonic acid diethyl ester* **5**. Yield 73%. MS (*m*/*z*, %): 288.1495 (57, M^+, calc. for $C_{14}H_{25}O_4P$ 288.14904), 273 (23), 260 (24), 246 (13), 245 (18), 220 (67), 219 (49), 217 (13), 208 (13), 192 (47), 191 (37), 178 (10), 165 (11), 163 (54), 152 (100), 138 (29), 125 (39), 122 (16), 121 (11), 111 (19), 109 (15), 108 (26), 107 (28), 97 (13), 93 (18), 82 (12), 81 (26); IR (ν_{max}/cm^{-1} in $CHCl_3$): 2900–3000 (C–H), 1707 (C=O), 1238 (P=O), 1138 (P–O–C), 1107 (P–O–C), 1057 (POC); NMR data (C_6D_6/CCl_4 = 1:5 v/v; 160 mg ml^{-1}): ^{1}H NMR (400.13 MHz) δ: 0.75 (s, 3H, H-8), 1.12 (d, J = 11.0 Hz, 1H, H-7α), 1.20 (t, J = 7.0 Hz, 6H, $POCH_2CH_3$), 1.22 (s, 3H, H-9), 1.42 (ddd, J = 18.0, 16.0, 11.0 Hz, 1H, H-10a), 1.96 (m, 1H, H-5), 2.37 (dd, J = 19.0, 2.5 Hz, 1H, H-4α), 2.42 (ddd, J = 6.5, 6.5, 2.5 Hz, 1H, H-1), 2.46 (d, J = 16.0 Hz, 1H, H-10b), 2.51 (ddd, J = 19.0, 4.0, 3.0 Hz, 1H, H-4β), 2.53 (m, 1H, H-7β), 2.55 (m, J_{PH} = 18.0 Hz, 1H, H-2), 3.93 (m, 4H, $POCH_2CH_3$); ^{13}C NMR (100.61 MHz) δ: 16.61 and 16.67 ($POCH_2CH_3$), 22.10 (C-8), 27.23 (C-9), 27.48 (J_{C-P} = 144.1 Hz, C-10), 34.47 (C-7), 39.11 (C-5), 39.21 (C-6), 43.00 (J_{C-P} = 1.5 Hz, C-1), 44.63 (J_{C-P} = 1.9 Hz, C-4), 50.80 (J_{C-P} = 3.4 Hz, C-2), 61.03 and 61.41 ($POCH_2CH_3$), 209.45 (J_{C-P} = 16.2 Hz, C-3); ^{31}P NMR (81.015 MHz) δ: 29.47.

‡ (1*R*,2*RS*,5*S*)-5-*Isopropenyl*-2-*methyl*-3-*oxocyclohexylphosphonic acid diethyl ester* **4**. Mixture of isomers **4a** and **4b** (1:3); yield 23%. $[\alpha]^{25}$ +15.9 (*c* 5.40, $CHCl_3$); MS (*m*/*z*, %): 288.1496 (6, M^+, calc. for $C_{14}H_{25}O_4P$ 288.14904), 179 (9), 151 (20), 150 (100), 139 (17), 135 (39), 123 (10), 111 (11), 55 (11); IR (ν_{max}/cm^{-1} in $CHCl_3$): 2900–3000 (CH), 1710 (C=O), 1638 (C=C), 1230 (P=O), 1050 (P–O–C), 1025 (P–O–C), 963 (P–O–C); ^{31}P NMR (81.015 MHz, C_6D_6/CCl_4 = 1:5 v/v, 160 mg ml^{-1}) δ: 29.82 and 30.66.

For **4a**: ^{1}H NMR (400.13 MHz, C_6D_6, 160 mg ml^{-1}) δ: 1.15 (d, J = 7.2 Hz, 3H, H-10), 1.19–1.28 (m, 6H, $POCH_2CH_3$), 1.69 (s, 3H, H-9), 1.71–2.54 (m, 6H), 2.72 (m, 1H, H-5), 3.90–4.05 (m, 4H, $POCH_2CH_3$), 4.68 (s, 1H, H-8b), 4.75 (s, 1H, H-8a); ^{13}C NMR (100.61 MHz, C_6D_6/CCl_4 = 1:5 v/v, 160 mg ml^{-1}) δ: 13.75 (J_{C-P} = 2.0 Hz, C-10), 16.51 (J_{C-P} = 6.3 Hz, $POCH_2CH_3$), 16.71 (J_{C-P} = 5.8 Hz, $POCH_2CH_3$), 21.31 (C-9), 29.81 (J_{C-P} = 3.3 Hz, C-6), 38.49 (J_{C-P} = 141.0 Hz, C-1), 41.66 (J_{C-P} = 6.7 Hz, C-5), 44.33 (C-4), 44.84 (J_{C-P} = 2.8 Hz, C-2), 61.11 (J_{C-P} = 6.9 Hz, $POCH_2CH_3$), 61.57 (J_{C-P} = 6.9 Hz, $POCH_2CH_3$), 111.13 (C-8), 147.07 (C-7), 206.91 (J_{C-P} = 6.0 Hz, C-3).

For **4b**: ^{1}H NMR (400.13 MHz, C_6D_6, 160 mg ml^{-1}) δ: 1.16 (d, J = 6.9 Hz, 3H, H-10), 1.19–1.28 (m, 6H, $POCH_2CH_3$), 1.68 (s, 3H, H-9), 1.71–2.54 (m, 6H), 2.72 (m, 1H, H-5), 3.90–4.05 (m, 4H, $POCH_2CH_3$), 4.65 (s, 1H, H-8b), 4.80 (s, 1H, H-8a); ^{13}C NMR (100.61 MHz, C_6D_6/CCl_4 = 1:5 v/v, 160 mg ml^{-1}) δ: 15.59 (J_{C-P} = 5.3 Hz, C-10), 16.81 (J_{C-P} = 6.3 Hz, $POCH_2CH_3$), 16.88 (J_{C-P} = 5.8 Hz, $POCH_2CH_3$), 21.88 (C-9), 27.49 (J_{C-P} = 4.0 Hz, C-6), 38.40 (J_{C-P} = 142.6 Hz, C-1), 41.01 (J_{C-P} = 11.7 Hz, C-5), 43.56 (C-4), 43.92 (J_{C-P} = 3.4 Hz, C-2), 61.36 (J_{C-P} = 6.5 Hz, $POCH_2CH_3$), 61.79 (J_{C-P} = 6.9 Hz, $POCH_2CH_3$), 112.46 (C-8), 146.39 (C-7), 208.34 (J_{C-P} = 12.4 Hz, C-3).

§ (1*S*,2*S*,3*S*,6*R*)-3,7,7-*Trimethyl*-4-*oxobicyclo*[4.1.0]*hept*-2-*ylphosphonic acid diethyl ester* **6**. Yield 90%. $[\alpha]^{22}$ +0.8 (*c* 3.81, $CHCl_3$); MS (*m*/*z*, %): 288.14892 (17, M^+, calc. for $C_{14}H_{25}O_4P$ 288.14904), 179.0 (100), 154.9 (44), 151.0 (22), 150.0 (33), 138.9 (37), 138.0 (26), 135.0 (22), 126.9 (24), 123.0 (18), 122.0 (17), 121.0 (15), 111.0 (67), 109.0 (38), 98.9 (38), 93.0 (43), 87.0 (21), 81.9 (29), 80.9 (35), 65.0 (24), 59.1 (18); IR (ν_{max}/cm^{-1} in $CHCl_3$): 2900–3000 (C–H), 1710 (C=O), 1240 (P=O), 1050 (P–O–C), 1025 (P–O–C), 964 (P–O–C); ^{1}H NMR (400.13 MHz, C_6D_6/CCl_4 = 1:2.5 v/v, 80 mg ml^{-1}) δ: 0.78 (ddd, J = 9.0, 9.0 5.0 Hz, 1H, H-6), 0.78 (s, 3H, H-8), 0.94 (s, 3H, H-9), 1.04 (ddd, J = 17.0, 9.0, 8.0 Hz, 1H, H-1), 1.15 (t) and 1.16 (t, J = 7.0 Hz, 6H, $POCH_2CH_3$), 1.19 (d, J = 7.0 Hz, 3H, H-10), 1.52 (ddd, J = 22.0, 12.0, 8.0 Hz, 1H, H-2), 1.94 (ddd, J = 17.5, 5.0, 3.0 Hz, 1H, H-5β), 2.27 (dd, J = 17.5, 9.0 Hz, 1H, H-5α), 2.37 (ddq, J = 12.0, 12.0, 7.0 Hz, 1H, H-3), 3.94 (m, 4H, $POCH_2CH_3$); ^{13}C NMR (50.32 MHz, C_6D_6/CCl_4 = 1:5 v/v, 100 mg ml^{-1}) δ: 14.30 (C-8), 15.16 (C-10), 16.84 and 16.94 (J_{C-P} = 4.9 Hz, $POCH_2CH_3$), 19.83 (J_{C-P} = 1.9 Hz, C-7), 21.59 (J_{C-P} = 7.2 Hz, C-1), 22.43 (J_{C-P} = 2.0 Hz, C-6), 28.19 (C-9), 35.46 (C-5), 37.47 (J_{C-P} = 143.2 Hz, C-2), 42.22 (J_{C-P} = 3.6 Hz, C-3), 61.20 and 61.85 (J_{C-P} = 6.8 Hz, $POCH_2CH_3$), 210.52 (J_{C-P} = 17.1 Hz, C-4); ^{31}P NMR (81.015 MHz, C_6D_6/CCl_4 = 1:5 v/v; 100 mg ml^{-1}) δ: 29.33.

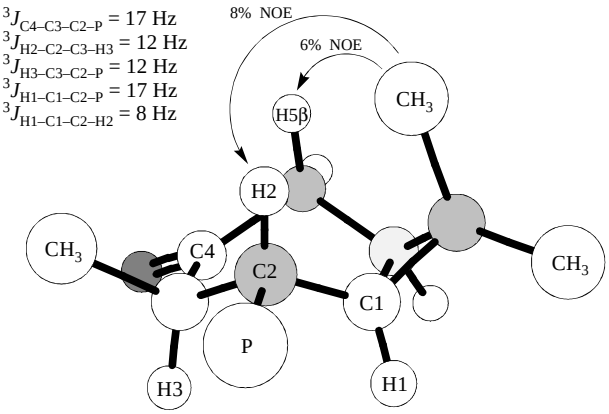
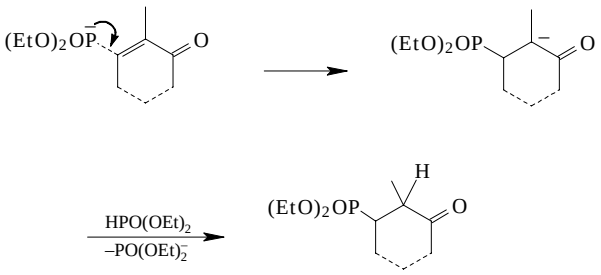


Figure 1 Selected spin–spin couplings and homonuclear Overhauser effects for compound **6**.

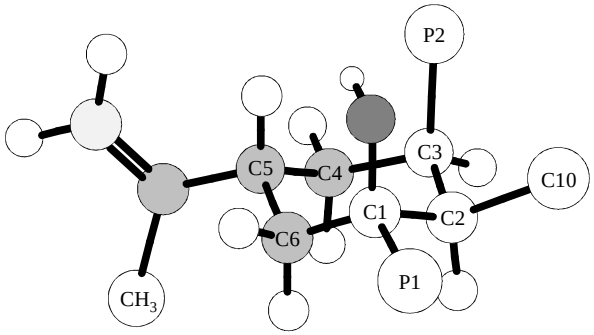
The reaction seems to proceed in accordance with the following scheme involving addition of diethylphosphite anion from the least hindered side of the conjugated carbon–carbon double bond followed by addition of a proton (derived from the diethylphosphite molecule) from the least hindered side of the resulting carbanion:



The reaction of carvone **1** results in formation of diphosphonate **7**¶ in significant amounts, while in the case of pinocarvone **2** and 2-caren-4-one **3** only impurities of the corresponding diphosphonates occur. Due to the good solubility of compounds of this type in concentrated aqueous alkalis, they are easily removed by washing of the reaction mixtures with 30% aq. NaOH. Diphosphonate **7** was isolated by liquid chromatography when washing with concentrated aqueous ammonia instead of sodium hydroxide solution.

Signal assignment in the NMR spectra of the new

¶ (1*R*,2*R*,3*R*,5*R*)-3-(*Diethoxyphosphoryl*)-1-*hydroxy*-5-*isopropenyl*-2-*methylcyclohexylphosphonic acid diethyl ester* **7**. Yield 63%. $[\alpha]^{22}$ –11.8 (*c* 2.38, $CHCl_3$); MS (*m*/*z*, %): 426.1944 (3, M^+, calc. for $C_{18}H_{36}O_7P_2$ 426.19361), 398 (9), 290 (15), 289 (100), 271 (24), 261 (9), 151 (28), 150 (22), 139 (19), 135 (10), 134 (9), 133 (25), 111 (16), 109 (33), 91 (10), 83 (12), 82 (9); IR (ν_{max}/cm^{-1} in $CHCl_3$): 2900–3000 (C–H), 1650 (C=C), 1238 (P=O), 1038 (P–O–C), 975 (P–O–C); NMR data (C_6D_6, 160 mg ml^{-1}): ^{1}H NMR (400.13 MHz) δ: 0.98 (t, J = 7.1 Hz, 6H, $POCH_2CH_3$), 1.10 (t, J = 7.1 Hz, 3H, $POCH_2CH_3$), 1.12 (t, J = 7.1 Hz, 3H, $POCH_2CH_3$), 1.30 (dddd, J = 39.8, 13.0, 13.0, 5.9 Hz, 1H, H-4ax), 1.60 (t, J = 1.4 Hz, 3H, H-9), 1.61 (d, J = 7.3 Hz, 3H, H-10), 1.83 (ddd, J = 13.0, 13.0, 4.2 Hz, 1H, H-6ax), 2.05 (m, J_{PH} = 7.2 Hz, 1H, H-4eq), 2.06 (m, J_{PH} = 28.1, 7.4 Hz, 1H, H-3), 2.48 (dqdd, J = 42.2, 7.3, 5.9, 4.2 Hz, 1H, H-2), 2.50 (dddd, J = 13.0, 6.2, 3.7, 2.8 Hz, 1H, H-6eq), 2.77 (m, J = 2×13.0, 1.8 Hz, $W_{1/2}$ = 7 Hz, 1H, H-5), 3.80–4.19 (m, 8H, $POCH_2CH_3$), 4.72 (q, J = 1.5 Hz, 1H, H-8a), 4.75 (m, 1H, H-8b); ^{13}C NMR (100.61 MHz) δ: 16.27 (J_{C-P} = 6.1 Hz, $POCH_2CH_3$), 16.37 (J_{C-P} = 5.5 Hz, $POCH_2CH_3$), 16.41 (J_{C-P} = 4.3, 2.1 Hz, C-10), 16.62 (J_{C-P} = 5.4 Hz, $POCH_2CH_3$), 20.73 (C-9), 32.39 (J_{C-P} = 1.5 Hz, C-4), 35.85 (J_{C-P} = 12.0, 2.1 Hz, C-5), 37.84 (J_{C-P} = 3.0, 2.2 Hz, C-2), 39.57 (J_{C-P} = 136.6, 16.7 Hz, C-3), 41.29 (J_{C-P} = 1.7 Hz, C-6), 61.40 (J_{C-P} = 7.2 Hz, $POCH_2CH_3$), 62.48 (J_{C-P} = 6.8 Hz, $POCH_2CH_3$), 62.55 (J_{C-P} = 6.6 Hz, $POCH_2CH_3$), 62.87 (J_{C-P} = 7.4 Hz, $POCH_2CH_3$), 75.67 (J_{C-P} = 170.7, 1.8 Hz, C-1), 109.66 (C-8), 149.11 (C-7); ^{31}P NMR (81.015 MHz, C_6D_6/CCl_4 = 1:5 v/v; 160 mg ml^{-1}) δ: 24.48 (P–C1), 36.48 (P–C3).



$^3J_{H4ax–C4–C3–P2}$ = 39.8 Hz
$^3J_{H4eq–C4–C3–P2}$ = 7.2 Hz
$^3J_{H6ax–C6–C1–P1}$ = 4.2 Hz
$^3J_{H6eq–C6–C1–P1}$ = 6.2 Hz
$^3J_{H2–C2–C1–P1}$ = 4.2 Hz
$^3J_{H2–C2–C3–P2}$ = 42.2 Hz
$^3J_{C3–C2–C1–P1}$ = 16.7 Hz
$^3J_{C1–C2–C3–P2}$ = 1.8 Hz
$^3J_{C5–C6–C1–P1}$ = 12.0 Hz
$^3J_{C5–C4–C3–P2}$ = 2.1 Hz
$^4J_{H3–C3–C2–C1–P1}$ = 7.4 Hz
$^3J_{C10–C2–C3–P2}$, $^3J_{C10–C2–C1–P1}$ } 4.3 and 2.1 Hz

Figure 2 Selected spin–spin couplings for diphosphonate **7**.

phosphorus-containing terpenic derivatives was made using 2D homonuclear *J*-resolved experiments, 2D H-H-COSY, C-H-COSY (J = 125 and 10 Hz) and nuclear Overhauser enhancement. Spin–spin couplings $J_{C–P}$ were taken from proton-decoupled ^{13}C spectra whereas spin–spin couplings $J_{H–P}$ were measured in 2D H-H *J*-resolved spectra. The stereochemistry of the new compounds was determined by comparison of the experimental spin–spin couplings with the calculated ones for different stereoisomers. Conformational analysis was carried out using molecular mechanics calculations (MM2) and semiempirical quantum-chemical calculations (PM3). Selected characteristic NMR parameters of phosphonates **6** and **7** are shown in Figures 1 and 2, respectively. Assignment of phosphorus resonances in compound **7** was made on the basis of the influence of substituents: electron acceptors at the α-carbon are known to induce high-field shifts of the ^{31}P nucleus.[17] In addition, phosphoryl oxygen at the axial phosphorus (at C-3) can form an intramolecular hydrogen bond with the hydroxyl, and this can result in a low-field shift of the phosphorus nucleus.[18] Compound **7** is formed from the corresponding monophosphonate **4**, therefore the primary monophosphonate is drawn as isomer **4a** with the same configuration of the secondary methyl group. Compound **5** was assigned to the isopinocamphone series (β-oriented substituent at C-2) based on comparison of the ^{13}C NMR spectrum of this molecule with the spectra of a number of related derivatives of pinocamphone and isopinocamphone types[19–21] and taking into account the minor β-effect of the phosphonate group.[18]

The authors thank The Competitive Center on Natural Sciences at the St. Petersburg University (grant no. 95-0-9.4-102) and the Russian Foundation for Basic Research (grant no. 96-03-33222) for financial support of this work.

References

1 N. A. Kardanov, S. A. Trifonova, N. N. Godovikov and M. I. Kabachnik, *Abstracts of the 6th International Congress of Pesticide Chemistry*, Hamburg, 1990, vol. 1, p. 16.
2 L. M. Abell and J. A. Kerschen, *Abstracts of the 7th International Congress of Pesticide Chemistry*, Washington, 1994, vol. 1, p. 306.
3 I. A. Nuretdinov, E. V. Bayandina and A. A. Schtyrlina, *Abstracts of the 7th International Congress of Pesticide Chemistry*, Washington, 1994, vol. 2, p. 901.
4 L. P. A. de Jong and H. P. Benschop, in *Stereoselectivity of Pesticides*, eds. E. J. Arins, J. J. S. van Rensen and W. Welling, Elsevier, Amsterdam, 1988, p. 109.
5 A. Fuchs, in *Stereoselectivity of Pesticides*, eds. E. J. Arins, J. J. S. van Rensen and W. Welling, Elsevier, Amsterdam, 1988, p. 203.
6 C. Giordano and C. Graziano, *J. Org. Chem.*, 1989, **54**, 1470.
7 G. Wilke, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 185.
8 V. V. Dudina and I. P. Beletskaya, *Zh. Org. Khim.*, 1992, **28**, 1929 (*Russ. J. Org. Chem.*, 1992, **28**, 1547).
9 E. D. Mihelich and D. J. Eickhoff, *J. Org. Chem.*, 1983, **48**, 4135.
10 R. E. Bozak and C. L. Hill, *J. Chem. Educ.*, 1982, **59**, 36.
11 T.-L. Ho and Z. U. Din, *Synth. Commun.*, 1980, **10**, 921.
12 T.-L. Ho and Z. U. Din, *US Patent*, 4296038, Cl. 260-343.21, 07D311/93, 1982 (*Chem. Abstr.*, 1982, **96**, 85797).
13 A. N. Pudovik, *Usp. Khim.*, 1954, **23**, 547 (in Russian).
14 A. N. Pudovik and I. V. Konovalova, *Synthesis*, 1979, 81.
15 D. Liotta, U. Sunay and S. Ginsberg, *J. Org. Chem.*, 1982, **47**, 2227.
16 E. A. Boyd, M. Corless, K. James and A. C. Regan, *Tetrahedron Lett.*, 1990, **31**, 2933.
17 D. G. Gorenstein, *Non-biological Aspects of Phosphorus-31 NMR Spectroscopy*, in *Progress in Nuclear Magnetic Resonance Spectroscopy*, 1983, vol. 16, part 1.
18 L. D. Quin, *The Heterocyclic Chemistry of Phosphorus: Systems Based on the Phosphorus–Carbon Bond*, Wiley-Interscience, New York, 1981.
19 G. V. Kalechits, N. G. Kozlov and T. K. Vjalimjau, *Zh. Org. Khim.*, 1987, **23**, 2377 [*J. Org. Chem. USSR* (*Engl. Transl.*), 1987, **23**, 2097].
20 P. A. Petukhov and A. V. Tkachev, *Mendeleev Commun.*, 1996, 64.
21 A. M. Chibiryaev, S. A. Popov and A. V. Tkachev, *Mendeleev Commun.*, 1996, 18.

Received: Moscow, 10th January 1997
Cambridge, 25th February 1997; Com. 7/00347A