Chinese Journal of Chemistry, **2004**, *22*, 1003—1007 **Article**

Synthesis of 2-Acyl-2*H*-1,2,3-diazaphospholes and Their Diels-Alder Reaction with Cyclopentadiene†

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2*H*-1,2,3-Diazaphospholes **3a**—**3h** were prepared from various ketone acylhydrazones and phosphorus trichloride in the presence of triethylamine. Compounds **3** underwent feasible hetero-Diels-Alder reactions with cyclopentadiene to afford the respective anellated [1,2,3]diazaphospholes **4a**—**4d** as well as **4a'**—**4d'** in moderate yields. The *endo* rule in the reaction was observed under kinetic control conditions.

Keywords 2*H*-1,2,3-diazaphosphole, cyclopentadiene, Diels-Alder reaction

Introduction

Diels-Alder reaction is of no doubt among the most widely used synthetic strategies for the construction of six-membered cyclic compounds.[1] Incorporation of heteroatoms in the diene and/or dienophile moieties offers also a powerful synthetic way to six-membered heterocycles.[2] Since their appearance about thirty years ago, two-coordinated trivalent phosphorous compounds have attracted much attention from various aspects. Especially in the last few years or so, the scope of the Diels-Alder reaction has been expanded by using compounds bearing a >C=P— functionality. Examples in this regard are phosphaalkenes,[3] heterophospholes[4] and anellated azaphospholes.[5] In most cases, these kinds of phosphorous compounds act as dienophiles, but in a few cases they also serve as heterodienes.[6] For example, 1*H*-1,3-benzoxaphosphole has been reported to undergo the Diels-Alder reaction with 2,3-dimethylbutadiene stereospecifically.[7] Similar observation was reported for 2-acetyl-1,2,3-diazaphospholes which form [2 + 4] cycloadducts with cyclopentadiene or isoprene, with the latter occurring regioselectively.[8,9] The reaction was usually performed in the presence of sulfur or methyl iodide. The role of the oxidizing agent is obviously to avoid the reversibility of cycloaddition and push the reaction in the forward direction by oxidizing the σ^3-P atom of the initially formed [2+4] cycloadducts.[7]

The high reactivity of the >C=P— functionality toward Diels-Alder reaction as well as the regioselectivity has also attracted much theoretical interests. A semiempirical PM3 calculation on the reaction of 1,3-azaphospholo[5,1-*a*]isoquinoline with isoprene has revealed that the reaction is isoprene$_{HOMO}$-azaphosphole$_{LUMO}$ controlled and thus falls into the Type I Diels-Alder reaction according to Sustmann's category.[7] On the other hand, recent computations on Diels-Alder reaction of phosphaethene with 1,3-butadiene and with isoprene at the UB3LYP/6-311+G** level lead to a stepwise pathway with open chain intermediates and the results can account for the high regioselectivities involved in the reactions.[10]

Considering the fact that anellated heterophospholes have been at the forefront of the search for novel phosphorus-containing fused heterocycles,[11] we have initiated a program of study on the synthesis and reactions of 2*H*-1,2,3-diazaphospholes. In this paper, we have improved the literature method and present a reliable and high yielding synthetic sequence. A range of diversely substituted *2H*-1,2,3-diazaphospholes were accessible starting from ketone hydrazones. Acting as excellent dienophiles, they were found to undergo smooth Diels-Alder reactions with cyclopentadiene stereospecifically, leading to novel 4,7-methanophosphorino-[1,2-*c*][1,2,3]diazaphospholes.

Experimental

Melting points were determined in open capillaries and uncorrected. Commercially available solvents were dried by standard methods prior to use. IR spectra were recorded on a Mattson Alpha-centauri FT-IR spectrometer, for solids in KBr discs and for liquids by placing a thin layer of the CCl_4 solution between two KBr discs, and absorptions are given in wavenumbers (cm^{-1}). NMR spectra were acquired in DMSO-d_6, or $CDCl_3$ solutions on a Bruker 500 or a Varian 400 spectrometer. The chemical shifts refer to TMS (internal) or 85% H_3PO_4 (external) as standards. Coupling constant (*J*) values are given in Hz. Satisfactory microanalysis (C ±0.20, H±0.20, N±0.30) was obtained for all new compounds. All the reactions were carried out under a

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nitrogen atmosphere with strict exclusion of moisture using oven-dried apparatus and glassware.

Synthesis of 2-acetyl-2*H*-1,2,3-diazaphospholes and 2-ethoxylcarbonyl-2*H*-1,2,3-diazaphospholes 3

To a well-stirred solution of PCl_3 (11.0 g, 80 mmol) in anhydrous CH_2Cl_2 (60 mL) was added hydrazone **1** (40 mmol) in portions. The mixture was stirred further till the solid disappeared. Et_3N (8.1 g, 80 mmol) was then slowly added with an external ice-bath cooling, and stirring was continued for a further 6 h. The mixture was filtered to remove the formed salt of Et_3N•HCl. The solvent and excess of PCl_3 were evaporated under reduced pressure and dried benzene (90 mL) was added to dissolve the residue. Additional Et_3N (4.0 g, 40 mL) was then added dropwise at 0 ℃ and the mixture was stirred for 8 h and then filtered. The solvent was evaporated under reduced pressure, and the residue was subjected to vacuum distillation giving the product **3** as pale yellow thick oils.

2-Acetyl-5-methyl-2*H*-1,2,3-diazaphosphole (3a): Yield 65%; b.p. 68—70 ℃/266 Pa; ^{1}H NMR ($CDCl_3$/TMS) δ: 2.48 (d, 3H, $^4J_{P,H}$=1.7 Hz, CH_3), 2.73 (s, 3H, $COCH_3$), 7.85 (d, 1H, $^2J_{P,H}$=44.0 Hz, P=CH); ^{31}P NMR ($CDCl_3$/85% H_3PO_4) δ: 237.8; ^{13}C NMR ($CDCl_3$/TMS) δ: 16.1 (d, $^3J_{P,C}$=2.5 Hz, CH_3), 22.4 (CO**C**H_3), 145.8 (d, $^1J_{P,C}$=36.6 Hz, P=C), 159.3 (d, $^2J_{P,C}$=12.2 Hz, C=N), 173.3 (d, $^2J_{P,C}$=12.2 Hz, C=O); MS *m/z* (%): 142 (M^+, 34), 43 (100).

2-Acetyl-5-phenyl-2*H*-1,2,3-diazaphosphole (3b): Yield 56%; b.p. 142—144 ℃/266 Pa; ^{1}H NMR ($CDCl_3$/TMS) δ: 2.81 (s, 3H, $COCH_3$), 7.37—7.88 (m, $5H_{arom}$), 8.38 (d, 1H, $^2J_{P,H}$=42.9 Hz, P=CH); ^{31}P NMR ($CDCl_3$/85% H_3PO_4) δ: 239.7; ^{13}C NMR ($CDCl_3$/TMS) δ: 23.5 (CH_3), 127.3 (*m*-C_{arom}), 128.4 (*o*-C_{arom}), 129.3 (*p*-C_{arom}), 130.4 (d, $^3J_{P,C}$=2.4 Hz, *ipso*-C_{arom}), 142.4 (d, $^1J_{P,C}$=37.6 Hz, P=C), 160.4 (d, $^2J_{P,C}$=12.2 Hz, C=N), 174.2 (d, $^2J_{P,C}$=10.9 Hz, C=O); MS *m/z* (%): 204 (M^+, 72), 162 (100).

2-Acetyl-5-*tert*-butyl-2*H*-1,2,3-diazaphosphole (3c): Yield 52%; b.p. 86—88 ℃/399 Pa; ^{1}H NMR ($CDCl_3$/TMS) δ: 1.35 [s, 9H, $C(CH_3)_3$], 2.74 (s, 3H, $COCH_3$), 8.03 (d, 1H, $^2J_{P,H}$=42.9 Hz, P=CH); ^{31}P NMR ($CDCl_3$/85% H_3PO_4) δ: 238.0; ^{13}C NMR ($CDCl_3$/TMS) δ: 22.9 (CO**C**H_3), 31.0 [(**C**$H_3)_3$C], 33.7 [$(CH_3)_3$**C**], 141.7 (d, $^1J_{P,C}$=36.5 Hz, P=C) ,171.4 (d, $^2J_{P,C}$=12.2 Hz, C=N), 175.4 (d, $^2J_{P,C}$=12.2 Hz, C=O); MS *m/z* (%): 184 (M^+, 36), 127 (100).

2-Acetyl-4,5-(1,3-propylene)-2*H*-1,2,3-diazaphosphole (3d): Yield 28%; b.p. 128—130 ℃/53 Pa; ^{1}H NMR ($CDCl_3$/TMS) δ: 2.20—2.64 (m, 6H, $3CH_2$), 2.68 (s, 3H, $COCH_3$); ^{31}P NMR ($CDCl_3$/85% H_3PO_4) δ: 224.6; ^{13}C NMR ($CDCl_3$/TMS) δ: 23.2, 24.1, 25.1 ($3CH_2$), 23.9 (CH_3), 160.2 (d, $^2J_{P,C}$=10.8 Hz, C=N), 161.0 (d, $^1J_{P,C}$=37.7 Hz, P=C), 173.9 (d, $^2J_{P,C}$=10.8 Hz, C=O); MS *m/z* (%): 168 (M^+, 51), 43 (100).

2-Ethoxylcarbonyl-5-methyl-2*H*-1,2,3-diazaphosphole (3e): Yield 36%; b.p. 110—112 ℃/53 Pa; ^{1}H NMR ($CDCl_3$/TMS) δ: 1.47 (t, 3H, ^3J = 7.1 Hz, OCH_2C**H**$_3$), 2.52 (d, 3H, $^4J_{P,H}$=1.6 Hz, CH_3), 4.54 (q, 2H, ^3J=7.1 Hz, O**C**H_2CH_3), 7.83 (d, 1H, $^2J_{P,H}$=44.1 Hz, P=CH); ^{31}P NMR ($CDCl_3$/85% H_3PO_4) δ: 232.5; ^{13}C NMR ($CDCl_3$/TMS) δ: 14.5 (OCH_2**C**H_3), 17.7 (CH_3), 59.3 (O**C**H_2CH_3), 140.3 (d, $^1J_{P,C}$=37.2 Hz, P=C), 157.4 (d, $^2J_{P,C}$=12.6 Hz, C=N), 160.3 (d, $^2J_{P,C}$=12.6 Hz, C=O); MS *m/z* (%): 172 (M^+, 28), 73 (100); HRMS calcd for $C_6H_9N_2O_2P$: 172.0402, found 172.0410.

2-Ethoxylcarbonyl-5-phenyl-2*H*-1,2,3-diazaphosphole (3f): Yield 27%; b.p. 158—160 ℃/40 Pa; ^{1}H NMR ($CDCl_3$/TMS) δ: 1.49 (t, 3H, ^3J = 7.1 Hz, OCH_2C**H**$_3$), 4.57 (q, 2H, ^3J = 7.1 Hz, O**C**H_2CH_3), 7.85—8.05 (m, $5H_{arom}$), 8.40 (d, 1H, $^2J_{P,H}$=44.2 Hz, P=CH); ^{31}P NMR ($CDCl_3$/85% H_3PO_4) δ: 234.9; ^{13}C NMR ($CDCl_3$/TMS) δ: 14.5 (OCH_2**C**H_3), 59.6 (O**C**H_2CH_3), 129.6 (*m*-C_{arom}), 130.3 (*o*-C_{arom}), 130.4 (*p*-C_{arom}), 131.3 (d, $^3J_{P,C}$=2.5, *ipso*-C_{arom}), 138.7 (d, $^1J_{P,C}$=37.7 Hz, P=C), 159.5 (d, $^2J_{P,C}$=12.2 Hz, C=N), 161.6 (d, $^2J_{P,C}$=10.8, C=O); MS *m/z* (%): 234 (M^+, 67), 162 (100); HRMS calcd for $C_{11}H_{11}N_2O_2P$: 234.0558, found 234.0550.

2-Ethoxylcarbonyl-5-*tert*-butyl-2*H*-1,2,3-diazaphosphole (3g): Yield 28%; b.p. 102—104 ℃/53 Pa; ^{1}H NMR ($CDCl_3$/TMS) δ: 1.39 [s, 9H, $C(CH_3)_3$], 1.46 (t, 3H, ^3J=7.1 Hz, OCH_2C**H**$_3$), 4.48 (q, 2H, ^3J=7.1 Hz, O**C**H_2CH_3), 7.99 (d, 1H, $^2J_{P,H}$=44.1 Hz, P=CH); ^{31}P NMR ($CDCl_3$/85% H_3PO_4) δ: 233.0; ^{13}C NMR ($CDCl_3$/TMS) δ: 15.9 (OCH_2**C**H_3), 31.9 [(**C**$H_3)_3$C], 33.2 [$(CH_3)_3$**C**], 60.4 (O**C**H_2CH_3), 140.8 (d, $^1J_{P,C}$=36.8 Hz, P=C), 170.3 (d, $^2J_{P,C}$=11.8 Hz, C=N), 171.0 (d, $^2J_{P,C}$=11.6 Hz, C=O); MS *m/z* (%): 214 (M^+, 41), 157 (100); HRMS calcd for $C_9H_{15}N_2O_2P$: 214.0871, found 214.0868.

2-Ethoxylcarbonyl-4,5-(1,3-propylene)-2*H*-1,2,3-diazaphosphole (3h): Yield 26%; b.p. 129—130 ℃/27 Pa; ^{1}H NMR ($CDCl_3$/TMS) δ: 1.46 (t, 3H, ^3J=7.1 Hz, OCH_2C**H**$_3$), 2.37—3.05 (m, 6H, $3CH_2$), 4.52 (q, 2H, ^3J =7.1 Hz, O**C**H_2CH_3); ^{31}P NMR ($CDCl_3$/85% H_3PO_4) δ: 220.2; ^{13}C NMR ($CDCl_3$/TMS) δ: 15.9 (OCH_2**C**H_3), 27.5, 28.3, 32.3 ($3CH_2$), 61.2 (O**C**H_2CH_3), 155.9 (d, $^1J_{P,C}$=38.8 Hz, P=C), 163.4 (d, $^2J_{P,C}$=12.2 Hz, C=N), 171.3 (d, $^2J_{P,C}$=12.2 Hz, C=O); MS *m/z* (%): 198 (M^+, 46), 73 (100); HRMS calcd for $C_8H_{11}N_2O_2P$: 198.0558, found 198.0566.

Synthesis of the *endo* cycloadducts 4

Cyclopentadiene (2.0 g, 30 mmol) was added dropwise in a period of 2 min to **3** (2.8 g, 20 mmol) at 15 ℃ under magnetic stirring, and the mixture was stirred further for 5 min. The mixture was allowed to stand in a refrigerator for about 1 h during which time the *endo* cycloadducts **4** crystallized and the resultant crystal was collected by filtration through a porous plate and washed with cold ether (5—6 mL). The product was dried in vacuum to afford the pure **4** in 65%—75% yields.

Synthesis of the *exo* cycloadducts 4'

A solution of **3** (2.8 g, 20 mmol) and cyclopentadiene (2.0 g, 30 mmol) in toluene (3 mL) was stirred at room temperature for 3 d. The precipitates were collected by filtration. The crude product was subjected to flash chromatography on silica gel eluting with a mixture of 1∶1 Et_2O/dichloromethane, and the solvents were removed by vacuum evaporation. The pale colored solids were filtrated, washed with cold ethanol (10 mL) and dried under vacuum to give the *exo* cycloadducts **4'** as white solids in 50%—75% yield.

(*Endo*)-1-acetyl-1,3*a*,4,7-tetrahydro-3-methyl-4,7-methanophosphorino[1,2-*c*][1,2,3]diazaphosphole (4a): Yield 65%; m.p. 67—69 ℃; ^{1}H NMR (DMSO-d_6/TMS) δ: 1.21—1.77 (m, 2H, CH_2), 1.99 (s, 3H, CH_3), 2.12 (s, 3H, $COCH_3$), 3.38—3.68 (m, 3H), 5.80—6.27 (m, 2H, 5,6-H); ^{31}P NMR (DMSO-d_6/85% H_3PO_4) δ: 52.5; ^{13}C NMR (DMSO-d_6/TMS) δ: 18.5 (CH_3), 23.6 (CO**C**H_3), 45.0 (d, $^2J_{C,P}$=19.8 Hz, CH_2), 46.7 (d, $^1J_{C,P}$=35.1 Hz, 7-C), 47.8 (d, $^2J_{C,P}$=3.0 Hz, 4-C), 57.3 (d, $^1J_{C,P}$=17.2 Hz, 3*a*-C), 131.7 and 135.8 (5-C, 6-C), 159.2 (d, $^3J_{C,P}$=2.0 Hz, 3-C), 171.3 (d, $^2J_{C,P}$=9.1 Hz, C=O); IR (KBr) ν: 1644 (C=O), 693 (C—P) cm^{-1}.

(*Exo*)-1-acetyl-1,3*a*,4,7-tetrahydro-3-methyl-4,7-methanophosphorino[1,2-*c*][1,2,3]diazaphosphole (4a'): Yield 46%; m.p. 104—106 ℃; ^{1}H NMR (DMSO-d_6/TMS) δ: 1.21—1.70 (m, 2H, CH_2), 1.99 (s, 3H, CH_3), 2.12 (s, 3H, $COCH_3$), 3.32—3.44 (m, 1H, 4-H), 3.48 (m, $^2J_{P,H}$=33.1 Hz, 3*a*-H), 3.66 (d, $^2J_{P,H}$=15.9 Hz, 1H, 7-H), 5.81—6.26 (m, 2H, 5,6-H); ^{31}P NMR (DMSO-d_6/85% H_3PO_4) δ: 49.0; ^{13}C NMR (DMSO-d_6/TMS) δ: 17.8 (CH_3), 23.6 (CO**C**H_3), 41.2 (CH_2), 43.2 (d, $^2J_{C,P}$=6.0 Hz, 4-C), 44.9 (d, $^1J_{C,P}$=33.8 Hz, 7-C), 57.5 (d, $^1J_{C,P}$=14.0 Hz, 3*a*-C), 134.1 and 137.5 (5-C, 6-C), 157.0 (d, $^2J_{C,P}$=4.1 Hz, 3-C), 173.2 (d, $^2J_{C,P}$=9.1 Hz, C=O); IR (KBr) ν: 1644 (C=O), 693 (C—P) cm^{-1}; MS *m/z* (%): 208 (M^+, 10), 66 (100), 143 (70); HRMS calcd for $C_{10}H_{13}N_2OP$: 208.0766, found 208.0759.

(*Endo*)-1-acetyl-1,3*a*,4,7-tetrahydro-3-phenyl-4,7-methanophosphorino[1,2-*c*][1,2,3]diazaphosphole (4b): Yield 72%; m.p. 84—86 ℃; ^{1}H NMR (DMSO-d_6/TMS) δ: 1.23—2.00 (m, 2H, CH_2), 2.23 (s, 3H, $COCH_3$), 3.51—3.55 (m, 3H), 6.61—7.70 (m, 2H, 5,6-H), 7.40—7.83 (m, 5H$_{arom}$); ^{31}P NMR (DMSO-d_6/85% H_3PO_4) δ: 57.8; ^{13}C NMR (DMSO-d_6/TMS) δ: 24.8 (CO**C**H_3), 46.1 (d, $^2J_{C,P}$=25.2 Hz, CH_2), 47.8 (d, $^1J_{C,P}$=35.8 Hz, 7-C), 48.9 (d, $^2J_{C,P}$=4.1 Hz, 4-C), 58.5 (d, $^1J_{C,P}$ = 19.0 Hz, 3*a*-C), 128.9 (*m*-C$_{arom}$), 129.4 (*o*-C$_{arom}$), 131.5 (*p*-C$_{arom}$), 134.9 (d, $^3J_{C,P}$ = 1.9 Hz, *ipso*-C$_{arom}$), 132.8 and 136.9 (5-C, 6-C), 158.6 (d, $^2J_{C,P}$=2.9 Hz, 3-C), 172.5 (d, $^2J_{C,P}$=9.0 Hz, C=O); IR (KBr) ν: 1675 (C=O), 692 (C—P) cm^{-1}.

(*Exo*)-1-acetyl-1,3*a*,4,7-tetrahydro-3-phenyl-4,7-methanophosphorino[1,2-*c*][1,2,3]diazaphosphole (4b'): Yield 70%; m.p. 116—118 ℃; ^{1}H NMR (DMSO-d_6/TMS) δ: 1.30—2.01 (m, 2H, CH_2), 2.23 (s, 3H, $COCH_3$), 3.53—3.57 (m, 3H), 6.61—7.71 (m, 2H, 5,6-H), 7.41—7.84 (m, 5H$_{arom}$); ^{31}P NMR (DMSO-d_6/85% H_3PO_4) δ: 54.3; ^{13}C NMR (DMSO-d_6/TMS) δ: 24.6 (CO**C**H_3), 43.3 (CH_2), 45.4 (d, $^2J_{C,P}$=7.0 Hz, 4-C), 46.6 (d, $^1J_{C,P}$=33.9 Hz, 7-C), 58.8 (d, $^1J_{C,P}$=15.2 Hz, 3*a*-C), 128.2 (*m*-C$_{arom}$), 128.8 (*o*-C$_{arom}$), 130.8 (*p*-C$_{arom}$), 134.4 (d, $^3J_{C,P}$=2.0 Hz, *ipso*-C$_{arom}$), 135.2 and 139.6 (5-C, 6-C), 156.4 (d, $^2J_{C,P}$=4.9 Hz, 3-C), 175.5 (d, $^2J_{C,P}$=9.0 Hz, C=O); IR (KBr) ν: 1674 (C=O), 691 (C—P) cm^{-1}; MS *m/z* (%): 204 (M^+−C_5H_6, 31), 133 (100), 162 (93), 77 (46); HRMS calcd for $C_{15}H_{15}N_2OP$-C_5H_6: 204.0453, found 204.0449.

(*Endo*)-1-acetyl-3-(*tert*-butyl)-1,3*a*,4,7-tetrahydro-4,7-methanophosphorino[1,2-*c*][1,2,3]diazaphosphole (4c): Yield 46%; m.p. 28—30 ℃; ^{1}H NMR (DMSO-d_6/TMS) δ: 1.09 [s, 9H, C(CH_3)$_3$], 1.23—1.87 (m, 2H, CH_2), 2.06 (s, 3H, $COCH_3$), 2.94—2.98 (m, 3H), 6.55—7.64 (m, 2H, 5,6-H) ; ^{31}P NMR (DMSO-d_6/ 85% H_3PO_4) δ: 50.0; ^{13}C NMR (DMSO-d_6/TMS) δ: 23.4 (CO**C**H_3), 29.7 [C(**C**H_3)$_3$], 39.1 [**C**(CH$_3$)$_3$], 45.1 (d, $^2J_{C,P}$=1.9 Hz, CH_2), 46.7 (d, $^1J_{C,P}$=35.2 Hz, 7-C), 48.3 (d, $^2J_{C,P}$=3.0 Hz, 4-C), 50.5 (d, $^1J_{C,P}$=15.9 Hz, 3*a*-C), 131.8 and 135.9 (5-C, 6-C), 162.3 (d, $^2J_{C,P}$=1.9 Hz, 3-C), 171.7 (d, $^2J_{C,P}$=8.9 Hz, C=O); IR (KBr) ν: 1699 (C=O), 704 (C—P) cm^{-1}.

(*Exo*)-1-acetyl-3-(*tert*-butyl)-1,3*a*,4,7-tetrahydro-4,7-methanophosphorino[1,2-*c*][1,2,3]diazaphosphole (4c'): Yield 32%; m.p. 46—48 ℃; ^{1}H NMR (DMSO-d_6/TMS) δ: 1.10 [s, 9H, C(CH_3)$_3$], 1.24—1.92 (m, 2H, CH_2), 2.20 (s, 3H, $COCH_3$), 2.87—3.20 (m, 3H), 6.53—7.66 (m, 2H, 5,6-H); ^{31}P NMR (DMSO-d_6/ 85% H_3PO_4) δ: 47.8; ^{13}C NMR (DMSO-d_6/TMS) δ: 23.4 (CO**C**H_3), 29.6 [C(**C**H_3)$_3$], 38.5 [**C**(CH$_3$)$_3$], 41.7 (CH_2), 43.1 (d, $^2J_{C,P}$=5.1 Hz, 4-C), 45.0 (d, $^1J_{C,P}$=32.8 Hz, 7-C), 50.6 (d, $^1J_{C,P}$=13.9 Hz, 3*a*-C), 133.8 and 137.2 (5-C, 6-C), 160.4 (d, $^2J_{C,P}$=4.0 Hz, 3-C), 172.9 (d, $^2J_{C,P}$=9.0 Hz, C=O); IR (KBr) ν: 1698 (C=O), 702 (C—P) cm^{-1}; MS *m/z* (%): 251 (M^++1, 13), 99 (100), 57 (38); HRMS calcd for $C_{13}H_{19}N_2OP$ + 1: 251.1235, found 251.1246.

(*Endo*)-8-acetyl-7,8-diaza-9-phosphatetracyclo[8.2.1.0^{2,6}.0^{2,9}]trideca-6(7),11-diene (4d): Yield 56%; m.p. 62—64 ℃; ^{1}H NMR (DMSO-d_6/TMS) δ: 1.25—1.59 (m, 2H, 13-H$_2$), 2.24—2.40 (m, 6H, 3CH$_2$), 2.68 (s, 3H, $COCH_3$), 2.99—3.94 (m, 2H, 2CH), 5.95—6.33 (m, 2H, 11,12-H); ^{31}P NMR (DMSO-d_6/85% H_3PO_4) δ: 46.6; ^{13}C NMR (DMSO-d_6/TMS) δ: 23.5 (CO**C**H_3), 25.1, 30.5, 37.4 (3CH_2), 43.1 (d, $^2J_{C,P}$=20.9 Hz, 13-C), 47.1 (d, $^1J_{C,P}$=33.9 Hz, 10-C), 52.7 (d, $^2J_{C,P}$=3.0, 1-C), 65.4 (d, $^1J_{C,P}$=17.8 Hz, 2-C), 132.0 and 135.9 (11-C, 12-C), 161.8 (d, $^2J_{C,P}$=2.0 Hz, 6-C), 171.4 (d, $^2J_{C,P}$=9.0 Hz, C=O); IR (KBr) ν: 1700 (C=O), 698 (C—P) cm^{-1}.

(*Exo*)-8-acetyl-7,8-diaza-9-phosphatetracyclo[8.2.1.0^{2,6}.0^{2,9}]trideca-6(7),11-diene (4d'): Yield 36%; m.p. 82—84 ℃; ^{1}H NMR (DMSO-d_6/TMS) δ: 1.29—1.55 (m, 2H, 13-H$_2$), 2.23—2.50 (m, 6H, 3CH$_2$), 2.59 (s, 3H, $COCH_3$), 3.11—3.76 (m, 2H, 2CH), 5.97—6.44 (m, 2H, 11, 12-H); ^{31}P NMR (DMSO-d_6/85% H_3PO_4) δ: 44.2; ^{13}C NMR (DMSO-d_6/TMS) δ: 23.3 (CO**C**H_3), 25.0, 30.5, 37.2 (3CH_2), 39.8 (13-C), 48.9 (d, $^2J_{C,P}$=5.9 Hz,

1-C), 49.3 (d, $^1J_{C,P}$=34.1 Hz, 10-C), 65.5 (d, $^1J_{C,P}$=13.8 Hz, 2-C), 135.3 and 138.4 (11, 12-C), 160.4 (d, $^2J_{C,P}$=4.9 Hz, 6-C), 174.3 (d, $^2J_{C,P}$=8.8 Hz, C=O); IR (KBr) ν: 1700 (C=O), 698 (C—P) cm^{-1}; MS *m/z* (%): 234 (M^+, 11), 169 (100), 127 (98); HRMS calcd for $C_{12}H_{15}N_2OP$: 234.0922, found 234.0929.

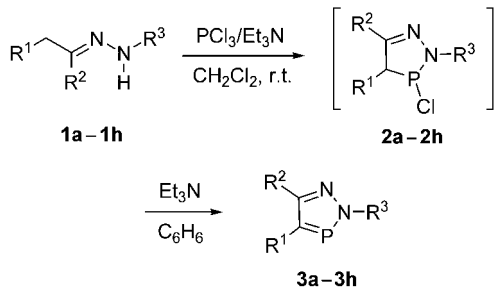
Results and discussion

Our present study began with the synthesis of 2-acyl substituted 2*H*-1,2,3-diazaphospholes **3** which served as the dienophiles. There are in principle two methods available for the synthesis of compounds **3**, both by employing the acylhydrazones **1** as the starting material.[9,12] One is to prepare firstly the 2-acyl-3-chloro-3,4-dihydro-2*H*-1,2,3-diazaphospholes **2** by reaction of the hydrazones **1** with two equivalents of phosphorus trichloride in the presence of two equivalents of triethylamine. Intermediates **2** are isolated and purified by crystallization from an appropriate solvent, and then allowed to react with another equimolecular amount of triethylamine affording, by elimination of HCl, the 2*H*-1,2,3-diazaphospholes **3**. The other one differs slightly from the above in that the intermediates **2** are not isolated from the reaction mixture, but directly transformed into **3** by further treatment with triethylamine.

We found that both methods suffer from some drawbacks. Using the first method gave only very poor overall yields of products owing to inconvenient handling, while using the second one resulted in the formation of **3** with contaminants. After screening a lot of reaction conditions we adapted the second one-pot strategy with slight variation for synthesizing **3**. The key lies in that the crude intermediates **2**, prepared by treating hydrazones **1** with phosphorus trichloride, filtering off the formed salt of NEt_3•HCl and evaporating the solvent and the excess PCl_3, were directly taken into dry benzene and subjected to further elimination of HCl with triethylamine. Using this procedure, we were able to synthesize diversely substituted compounds **3a**—**3h** in moderate to acceptable yields (Scheme 1). All the compounds were characterized by spectral analytical data.

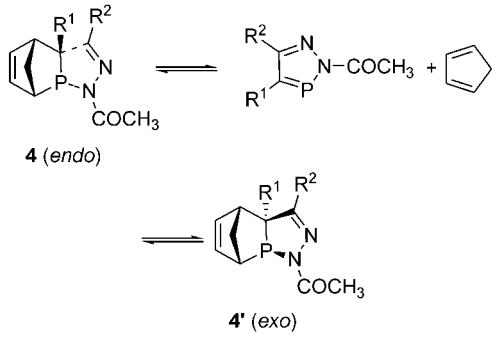
The 2-acetyl substituted compounds **3a**—**3d** were tested for Diels-Alder reactions with cyclopentadiene. It is well known that when the diene is a cyclic one, there are two possible addition ways for unsymmetrical dienophiles. The addition is predominantly *endo* with few exceptions. In the present study, compounds **3** undergo facile Diels-Alder reactions at the >C=P— functionality with cyclopentadiene. Both the *endo* and *exo* adducts (**4** and **4'**) can be obtained depending on the reaction conditions. It was observed that the reaction of **3** with cyclopentadiene at room temperature gave exclusively the *endo* adducts **4** in 65%—75% yields if the reaction was quenched after 5 min of stirring. However, prolonging the reaction time to 3 d the reaction led to the formation of *exo* adducts **4'** in 50%—75% yields. This behavior is just what one would expect in terms of the reversibility of this hetero-Diels-Alder reaction. In a shorter time, the reaction furnished the less stable *endo* adducts **4** under kinetic control, but under prolonged stirring, the more stable *exo* adducts **4'** were formed under thermodynamic control (Scheme 2).

Scheme 1



Product	R^1	R^2	R^3	Yield/%
3a	H	Me	$COCH_3$	65
3b	H	Ph	$COCH_3$	56
3c	H	*t*-Bu	$COCH_3$	52
3d	—$(CH_2)_3$—		$COCH_3$	28
3e	H	Me	$CO_2C_2H_5$	36
3f	H	Ph	$CO_2C_2H_5$	27
3g	H	*t*-Bu	$CO_2C_2H_5$	28
3h	—$(CH_2)_3$—		$CO_2C_2H_5$	26

Scheme 2



Product	R^1	R^2	Yield/%
4a, **4a'**	H	CH_3	65, 46
4b, **4b'**	H	Ph	72, 70
4c, **4c'**	H	*t*-Bu	46, 32
4d, **4d'**	—$(CH_2)_3$—		56, 36

The cycloadducts are novel kind of anellated heterophospholes,[11] appear as yellow to brownish crystalline solids and all have been characterized by spectral and analytical data. In the precursors **3**, highly deshielded ^{31}P NMR signals were found in the range of δ 220—240, characteristic for heterophospholes with an adjacent

nitrogen atom.[13] For each of the adducts **4** and **4'**, the chemical shifts around δ 44—58 in the ^{31}P NMR spectra are typical for three-coordinate phosphorus σ^3 atom.[9] This indicates clearly the change of hybridization and coordination state of phosphorus atom after [2 + 4] cycloaddition. In the ^{1}H NMR spectra, the multiplets between δ 2.9—3.7 are due to the methine protons while a multiplet in the range of 5.8—7.7 is for the two olefinic protons.

The characteristic feature of the ^{13}C NMR spectra of the products **4** and **4'** is the coupling of the heterophosphole ring carbons with phosphorus atom. The magnitudes were observed as follows: for the one bond P—C-7 coupling 33—34 Hz, for the one bond P—C-3a coupling 14—15 Hz, for the two bond P—C-4 coupling 5—7 Hz, and for the two bond P—C-3 coupling 4—5 Hz. The ^{13}C NMR absorptions for the carbonyl carbon were found in the range of δ 174—175 which appear as doublet due to the coupling with phosphorus ($^2J_{CP}$=9 Hz). Remarkably, the *endo* and *exo* structural assignments have been easily performed by inspection of the ^{13}C NMR signal of the bridging CH_2 group. In the *endo* form **4**, the CH_2 group is *cis* located with respect to the unshared electron pair of the P atom and gives a doublet at δ 43—46. However, because the CH_2 group becomes *trans* to the unshared electron pair of the P atom in the *exo* form **4'**, the signal was observed to be slightly upshielded by about δ 3 and no coupling with phosphorus could be found. An X-ray crystal structure study for the *exo* adducts **4a'** has been published by Breen[14] that is in agreement with our assignment.

In conclusion, we have reported a reliable procedure for the preparation of 2*H*-2-acyl-1,2,3-diazaphospholes **3a**—**3h** by treatment of ketone acylhydrazones **1a**—**1h** and phosphorus trichloride in the presence of triethylamine. The reactivity of the >C=P— functionality toward Diels-Alder reaction with cyclopentadiene has been investigated using the 3-acetyl substituted 2*H*-1,2,3-diazaphospholes **3a**—**3d** as representatives. Depending on reaction conditions, both the *endo* and *exo* anellated [1,2,3]diazaphospholes (**4a**—**4d** and **4a'**—**4d'**) can be obtained in moderate yields.

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