Synthesis of 9-Acetyl-8,9-diaza-1-phosphabicyclo[4.3.0]nona-3,7-dienes by Regioselective Diels–Alder Reaction of 2*H*-1,2,3-Diazaphospholes with Isoprene

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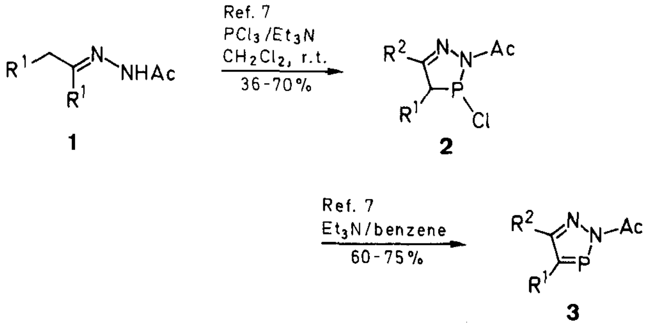
2*H*-1,2,3-Diazaphospholes, prepared from various hydrazones and phosphorus trichloride in the presence of triethylamine, react with isoprene to give highly regioselective Diels–Alder products in good yield.

Great attention has been paid to the study of two-coordinated trivalent phosphorus compounds since their appearance 20 years ago. Although some outstanding work has been done on the synthesis of 1,2,3-diazaphospholes, and their reactions with 1,3-dipolar compounds[1] little is known about their reactivity with other reagents, such as 1,3-dienes. Symmetric dienes have been used successfully with 1,2,3-diazaphospholes in Diels–Alder reactions,[2,3] but unsymmetric dienes have not been studied. We have reported earlier[4–6] on the syntheses of a series of 1,2,3-diazaphospholes, and their reactions with e. g. propargylic alcohol and catechol. In



1-3	R^1	R^2	1-3	R^1	R^2
a	H	Me	**c**	H	Ph
b	H	*t*-Bu	**d**	–$(CH_2)_2$–	

Scheme 1

Table 1. Compounds **2** and **3** Prepared

Product[a]	Yield (%)[b]	mp (°C)[c] or bp (°C)/Torr	Molecular Formula[d]	IR (KBr) ν (cm^{-1})	^{1}H-NMR ($CDCl_3$/TMS), δ, J (Hz)	^{13}C-NMR ($CDCl_3$/TMS), δ, J (Hz)	^{31}P-NMR ($CDCl_3$)[e], δ	MS (M^+) m/z (%)
2b	39	100–102	$C_8H_{14}ClN_2OP$ (220.6)	1699 (C=O), 436 (P–Cl)	1.32 (s, 9H, *t*-C_4H_8), 2.38 (d, 3H, $J_{P,H}$ = 1.8, $COCH_3$), 3.22 (d, 2H, $J_{P,H}$ = 22, PCH_2)	–	106.34	220 (3)
2c	71	112–115	$C_{10}H_{10}ClN_2OP$ (240.6)	1676 (C=O), 432 (P–Cl)	2.55 (d, 3H, $J_{P,H}$ = 1.8, $COCH_3$), 3.61 (d, 2H, $J_{P,H}$ = 22, PCH_2), 7.10–7.80 (m, 5H_{arom})	–	104.46	240 (4)
2d	37	99–101	$C_8H_{12}ClN_2OP$ (218.6)	1700 (C=O), 434 (P–Cl)	2.30 (m, 9H, 4 × CH_2 + PCH), 2.40 (d, 3H, $J_{P,H}$ = 1.8, $COCH_3$)	–	128.69	218 (15)
3b	75	86–88/3	$C_8H_{13}N_2OP$ (184.2)	–	1.34 (s, 9H, *t*-C_4H_9), 2.72 (s, 3H, $COCH_3$), 8.03 (d, 1H, $J_{P,H}$ = 43.2, P=CH)	22.43 ($CO\underline{C}H_3$), 30.01 [s, $(\underline{C}H_3)_3C$], 33.86 [s, $(CH_3)_3\underline{C}$], 141.18 (d, $J_{P,C}$ = 36.6, P=C), 171.30 (d, $J_{P,C}$ = 12.2, C=N), 174.11 (d, $J_{P,C}$ = 12.2, C=O)	238.00	184 (38)
3c	59	142–143/2	$C_{10}H_9N_2OP$ (204.2)	–	2.70 (s, 3H, $COCH_3$), 7.30–7.88 (m, 5H_{arom}), 8.26 (d, 1H, $J_{P,H}$ = 43.2, P=CH)	22.10 (s, CH_3), 126.33 (s, *m*-C_{arom}), 128.44 (s, *o*-C_{arom}), 128.99 (s, *p*-C_{arom}), 131.92 (d, $J_{P,C}$ = 2.44, C_{arom}), 140.66 (d, $J_{P,C}$ = 37.8, P=C), 160.14 (d, $J_{P,C}$ = 12.2, C=N), 173.54 (d, $J_{P,C}$ = 10.9, C=O)	239.75	204 (79)
3d	60	128–130/0.4	$C_8H_{11}N_2OP$ (182.2)	–	2.41 (m, 8H, 4 × CH_2), 2.68 (s, 3H, $COCH_3$)	22.27, 22.92, 23.46, 25.03 (4 × CH_2), 22.39 (s, CH_3), 159.19 (d, $J_{P,C}$ = 10.9, C=N), 160.05 (d, $J_{P,C}$ = 37.8, P=C), 173.67 (d, $J_{P,C}$ = 10.9, C=O)	224.67	182 (58)

[a] Compounds **2a** and **3a** were prepared according to Ref. 7.
[b] Yield of isolated product.
[c] Recrystallized from petroleum ether (bp 30–60 °C)/Et_2O.
[d] Satisfactory microanalyses obtained: C ±0.37, H ±0.34, N ±0.25.
[e] 85% H_3PO_4 was used as an external standard.

Table 2. Compounds **4** Prepared

Product	Yield[a] (%)	mp (°C)[b]	Molecular Formula[c]	^{1}H-NMR ($CDCl_3$/TMS) δ, J (Hz)	^{31}P-NMR ($CDCl_e$)[d] δ
4a	82	75–77	$C_{10}H_{15}N_2OP$ (210.2)	1.70 (s, 3H, C=CCH_3), 1.96 (s, 3H, N=CCH_3), 2.06 (m, 2H, PCH_2), 2.23 (s, 3H, $COCH_3$), 2.60 (m, 2H, CH_2), 3.40 (dt, 1H, $J_{H,H}$ = 3.6, $J_{P,H}$ = 36.5, PCH), 5.50 (m, 1H, =CH)	38.90
4b	80	39–42	$C_{13}H_{21}N_2OP$ (252.3)	1.24 (s, 9H, t-C_4H_9), 1.72 (s, 3H, C=CCH_3), 1.99 (m, 2H, PCH_2), 2.24 (s, 3H, $COCH_3$), 2.75 (m, 2H, CH_2), 3.60 (dt, 1H, $J_{H,H}$ = 3.6, $J_{P,H}$ = 36.5, PCH), 5.52 (m, 1H, =CH)	47.11
4c	91	110–112	$C_{15}H_{17}N_2OP$ (272.3)	1.72 (s, 3H, C=CCH_3), 1.97 (m, 2H, PCH_2), 2.36 (s, 3H, $COCH_3$), 2.69 (m, 2H, CH_2), 4.08 (dt, 1H, $J_{H,H}$ = 3.6, $J_{P,H}$ = 36.5, PCH), 5.34 (m, 1H, =CH), 7.30–7.80 (m, 5H_{arom})	50.07
4d	82	122–124	$C_{13}H_{19}N_2OP$ (250.3)	1.72 (s, 3H, C=CCH_3), 2.24 (s, 3H, $COCH_3$), 2.47 (m, 12H, 6 × CH_2), 5.55 (m, 1H, =CH)	62.73

[a] Yield of isolated product.

[b] Recrystallized from benzene/petroleum ether (bp 60 ~ 90 °C).

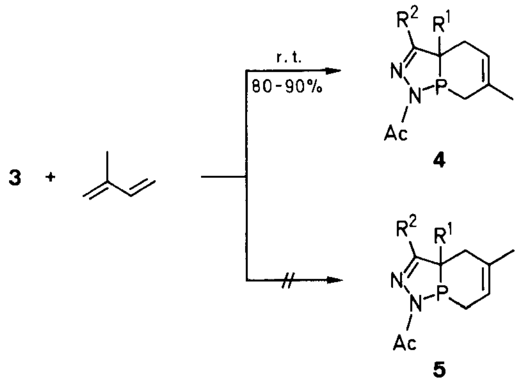
[c] Satisfactory microanalyses obtained: C ± 0.36, H ± 0.36, N ± 0.20.

[d] 85% H_3PO_4 was used as the external standard.

this paper, the reaction of isoprene with 2H-1,2,3-diazaphospholes as dienophiles is described.

Substituted 2H-1,2,3-diazaphospholes **3** were synthesized by the reaction of phosphorus trichloride with hydrazones **1** in the presence of triethylamine (Scheme **1**). The new compounds were characterized by spectral and analytical data (Table 1).

In order to study the reaction of 1,2,3-diazaphospholes with unsymmetric dienes, we carried out the reaction of **3** with isoprene, which gave only a single product **4** (Table 2). This regioselectivity is in good accordance with qualitative molecular orbital consideration[8] if phosphorus–carbon double bond is treated as a dienophile moiety. No trace of the isomeric adduct **5** was detected (Scheme **2**).



4	R^1	R^2	**4**	R^1	R^2
a	H	Me	**c**	H	Ph
b	H	t-Bu	**d**	–$(CH_2)_4$–	

Scheme 2

Melting points were determined with Thomas-Hover capillary melting point apparatus and are uncorrected. ^{1}H-, ^{13}C-, and ^{31}P-NMR spectra were obtained using a JEOL FX-90Q spectrometer. Microanalyses were obtained using a YANACO CHN CORDER MT-3 instrument. IR spectra were recorded on using a Nicolet 170 SX-FTIR spectrometer. Mass spectra were obtained using a VG.ZAB-HS spectrometer with EI ionization at 70 eV. All the solvents were dried and freshly distilled. All the reactions were carried out in a N_2 atmosphere. Compounds **2a** and **3a**, were prepared according to Ref. 7. Isoprene is available commercially.

2-Acetyl-3-chloro-3,4-dihydro-2H-1,2,3-diazaphospholes 2; General Procedure:[6]

In a dried 250 mL 4-necked round-bottomed flask fitted with a stirrer and an addition funnel, PCl_3 (27.4 g, 200 mmol) and CH_2Cl_2 (150 mL) are placed. Hydrazone **1** (100 mmol) is added in portions to the mixture with vigorous stirring till the solid disappears, then Et_3N (20.2 g, 200 mmol) is added dropwise below 20 °C. The mixture is stirred for 6 h and filtered. The solvent and excess of PCl_3 are removed *in vacuo* and the residue is extracted with Et_2O or Et_2O/petroleum ether (bp 30–60 °C) (3 × 25 mL) and the combined extracts are placed in a refrigerator. The crystals appeared are filtered and dried in vacuum to afford **2** (Table 1).

2-Acetyl-2H-1,2,3-diazaphospholes 3: General Procedure:

To a 100 mL 4-necked flask containing **2** (20 mmol) and benzene (70 mL) is added dropwise Et_3N (2.02 g, 20 mmol) below 10 °C. The mixture is stirred for 8 h and filtered. The solvent is evaporated at reduced pressure and the residue is distilled in vacuum to afford **3** (Table 1).

9-Acetyl-8,9-diaza-1-phosphabicyclo[4.3.0]nona-3,7-dienes 4; General Procedure:

A mixture of isoprene (0.55 g, 8.3 mmol) and **3** (8.3 mmol) is stirred vigorously at r.t. until it solidifies. The crude solid formed is recrystallized from benzene/petroleum ether (bp 60 ~ 90 °C) filtered, and dried in vacuum to afford **4** (Table 2).

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