1,3-Dipolar Cycloadditions of 9-Diazofluorenes and Diphenyldiazomethane to 2-Acyl-2*H*-1,2,3-diazaphospholes

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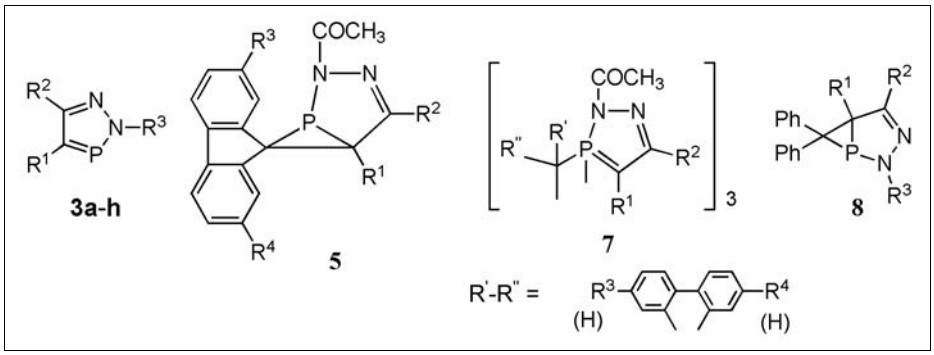

A series of 2-acyl-2*H*-1,2,3-diazaphospholes **3** underwent ready 1,3-dipolar cycloaddition reactions with 9-diazofluorenes as the 1,3-dipole, yielding the respective bicyclic phosphiranes **5** or trimers **7** depending on the reaction conditions employed. The reaction is believed to proceed *via* the formation of the [3+2]-cycloaddition adducts followed by elimination of nitrogen from the cyclic azo moiety. In the case of **3c**, the phosphatetraazabicyclooctadiene compound **6** has been isolated with no loss of nitrogen. Likewise, the dipolar cycloaddition reaction of diphenyldiazomethane with the >C=P- moiety as the 1,3-dipolarophile gave phosphadiazabicyclohexenes **8** in 32-68% yields.

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Introduction.

1,3-Dipolar cycloaddition has proved to be an effective synthetic tool, providing one of the best ways to construct five-membered heterocyclic compounds with diverse functionality [1]. In most cases, the reaction proceeds with controlled stereospecifity and regioselectivity with respect to the dipolarophiles. Apart from the common alkenes and alkynes, numerous heteroatom-containing unsaturated compounds have been developed and applied successfully as dienophiles, thus widening the scope of 1,3-dipolar cycloadditions considerably.

Two-coordinated trivalent phosphorus compounds, which appeared about thirty years ago, have earned ever-increasing research interests from various perspectives [2,3]. In this context, compounds that bear a >C=P- functionality, including phosphaalkenes [4,5], heterophospholes [5], phosphinines [6] and anellated azaphospholes [7], have received much attention. It has been shown that many >C=P- compounds are reactive toward Diels-Alder (DA) reaction with electron-rich 1,3-dienes. With unsymmetrical diene like isoprene the reaction occurs mostly in a high regioselective manner and the sense of the cycloaddition was governed by the relative coefficients of the frontier orbitals. For example, complete regioselectivity has been reported in the DA reaction of 2-acetyl-2*H*-1,2,3-diazaphosphole with isoprene [8]. Aside from phosphaalkenes that are known to undergo [2+4] cycloadditions under mild conditions, the similar ability of various heretophospholes to take part in DA reactions with 1,3-dienes may be attributed to the similarity of their frontier orbitals. However, such similarities are limited as phosphaalkenes have energetically closely spaced π- and σ orbitals (*i.e.* HOMO and the next HOMO) [9], whereas benzoxaphospholes, for instance, have a 10π-delocalized ring system with all the three highest occupied MOs being π-orbitals [10]. On the other hand, the P atom of anellated heterophospholes with high π-electron density tend to act as a [1+4]cheletropic center and react with heterodienes such as α-diketones and α-diimines to give the spirocyclic adducts [11,12].

In comparison to the study on the reactivity toward DA reactions, the exploration of heterophospholes for use as a dipolarophile in 1,3-dipolar cycloaddition reactions are seemingly not as plentiful. Exceptions are organic azides which have been repeatedly examined in the reactions with compounds containing a >C=P- functionality [3]. It has been demonstrated that phospha-alkenes including

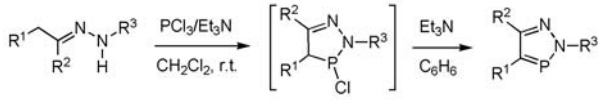
1,2,3-diazaphospholes can couple with organic azides either by the [2+3] cycloaddition reaction or in the Staudinger mode depending on the structure of substrates and reaction conditions. Also 1,2,3-diazaphospholes have been reported by Arbuzov's group and other researchers to react with diazoalkanes, giving out mainly the 1:1 cycloadducts *via* a [2+3]cycloaddition reaction [13]. However, the initial adducts are generally unstable and decompose under elimination of nitrogen leading to formation of a mixture of σ^3P compounds or cyclic trimer.

In connection with our recent interests on the reactivity of >C=P- functionality, we initiated a program on the synthesis of diversely substituted 2*H*-1,2,3-diazaphospholes and their reactions with 9-diazofluorene or diphenyldiazomethane as an 1,3-dipole molecule. We could show that the reaction can proceed in several directions and that the bicyclic phosphiranes or the cyclic trimers can be achieved will loss of nitrogen from the initial adducts. In one case, the "intact" 1,3-dipolar cycloadduct has been obtained.

Results and Discussion.

Our study began with the preparation of *2H*-1,2,3-diazaphospholes **3**. A literature survey suggested that methods for the synthesis of compounds **3** fall into two categories, both by employment of the acylhydrazones **1** as the starting material [8,14]. The first one features a two-sep synthesis in which the hydrazones **1** were allowed to react with two equivalents of phosphorus trichloride in the presence of two equivalents of triethylamine giving firstly the 2-acyl-3-chloro-3,4-dihydro-2*H*-1,2,3-diazaphospholes **2**. Intermediates **2** are isolated, purified and then treated with another equimolecular amount of triethylamine to afford the 2*H*-1,2,3-diazaphospholes **3**. In the other procedure isolation of the intermediates **2** is not effected. Both methods have been tested in the present study. After screening the reaction conditions, the second one-pot strategy with slight variation appears to be attractive for synthesizing **3**. The trick lies in that the intermediates **2**, generated by reaction of hydrazones **1** with PCl_3, filtering off the precipitated salt of NEt_3·HCl and removal of the solvent and the excess PCl_3 by vacuum distillation, were directly taken into dry benzene and treated

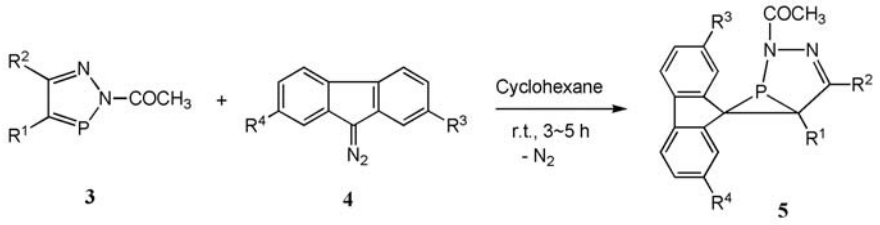
Scheme 1



1a-h **2a-h** **3a-h**

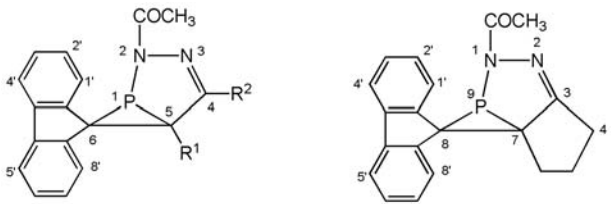
1-3	R^1	R^2	R^3	Yield (%)
a	H	Me	$COCH_3$	65
b	H	Ph	$COCH_3$	56
c	H	*t*-Bu	$COCH_3$	52
d		$-(CH_2)_3-$	$COCH_3$	28
e	H	Me	$CO_2C_2H_5$	36
f	H	Ph	$CO_2C_2H_5$	27
g	H	*t*-Bu	$CO_2C_2H_5$	28
h		$-(CH_2)_3-$	$CO_2C_2H_5$	26

Scheme 2



3 **4** **5**

5	R^1	R^2	R^3	R^4	Yields (%)
a	H	Me	H	H	77
b	H	Ph	H	H	90
c		$-(CH_2)_3-$	H	H	83
d	H	Ph	Cl	Cl	82
e	H	Ph	Br	Br	89

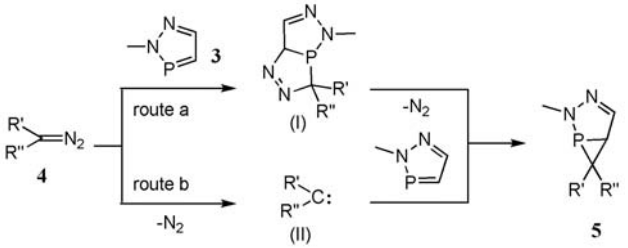


with another equivalent of triethylamine to eliminate the remaining HCl. Thus, employing this varied procedure, the diversely substituted *2H*-1,2,3-diazaphospholes **3a**-**h** were obtained in 26-65% yields (Scheme 1).

The reaction of **3a** with 9-diazofluorene was used as a model reaction to investigate the optimal condition. To a well-stirred solution of 9-diazofluorene **4a** in dry cyclohexane was added an equimolecular amount of **3a**. The reaction proceeded smoothly at room temperature. TLC analysis indicated that the reaction was successfully completed upon stirring for approximate 3 hours. Usual work-up furnished the phosphadiazabicyclohexene **5a** as a pale yellow powder in 77% yield (Scheme 2) with release of a N_2 molecule. Further elongating the reaction time or elevating the temperature gave inferior results.

Under the optimized conditions, the dipolar cycloaddition of 9-diazofluorene **4a** with *2H*-1,2,3-diazophospholes **3b** and **3c** gave the respective phosphadiazabicyclohexene **5b** and tricyclic **5c**, respectively. Similarly, from the dihalogenated 9-diazofluorenes **4d** and **4e** the corresponding 2′,7′-dihalo substituted analogues **5d** and **5e** were obtained in high yields (Scheme 2).

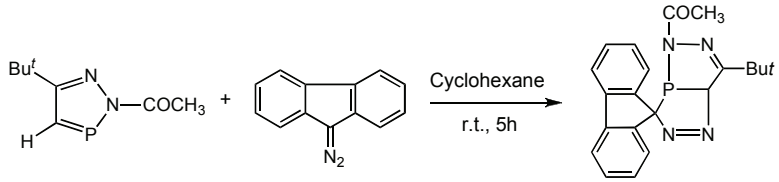
Scheme 3



However, for the reaction of the 2*H*-1,2,3-diazophosphole **4a** **3c** with 9-diazafluorene no elimination of nitrogen occurred and the respective 3-spiro-substituted *3H*-1,2,4-diazaphospholo fused 1,2,3-diazaphosphole **6** has been isolated in 65% yield after stirring for five hours at room temperature as a grayish powder. This may be attributed to the stabilizing effect exerted by the congested tertiary butyl substitutent at 7-position of **6** (Scheme 4).

The reaction can also be performed in a polar solvent like dichloromethane, but the isolated products proved to be cyclic trimer compounds **7**. Thus, 9-diazofluorene **4a** reacted with the *2H*-1,2,3-diazaphosphole **3a** *via* a [2+3] cycloaddition

Scheme 4



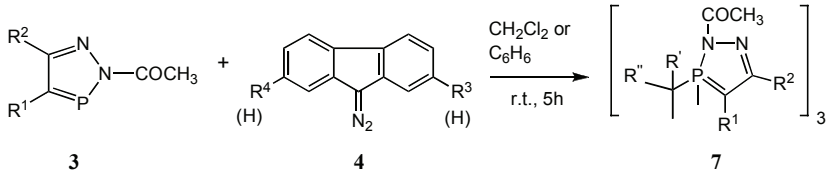
3c **4a** **6**

Scheme 3 tries to explain the above reactions. The initial step is a typical 1,3-dipolar cycloaddition of 9-diazofluorene as the 1,3-dipole with the *2H*-1,2,3-diazaphosphole serving as the dipolarophile. The cycloaddition across the >C=P- double bond provides the primary adducts I. Intermediates I are characteristic of pyrazolines, which are labile and prone to eliminating nitrogen to give the phosphirane-fused heterocycles **5a**-**e** as the final products. The elimination of nitrogen from cyclic azo compounds is one of the most widely used procedures, especially for the synthesis of strained-ring systems [15]. Our results are comparable to those observed for the reaction between diazo compounds with alkenes [16]. It has been repeatedly reported that the initially formed pyrazolines undergo thermal or photochemical loss of nitrogen to yield various cyclopropanes. Although the possibility *via* formation of carbene species (II) cannot be rigorously excluded, the fact that none of cycloadducts onto the >C=N- double bonds has been detected from the product led us prefer route a as the plausible way.

reaction to give the cyclic trimer **7a** in 95% isolated yield. In a similar manner, other cyclic trimers were prepared in high to excellent yields, except for **3c** which provided **7c** in only 56% yield due to the steric effect of tertiary butyl group (Scheme 5). This phenomenon is reminiscent of the observations made by Appel who reported that the products of 1,3-dilopar cycloaddition of phosphaalkenes with azides could eliminate nitrogen to give the dimer diazadiphosphetidines as final products [17]. The same thing happens if the reaction is carried out in dry benzene, affording also the cyclic trimers.

Mechanistically, the formation of the cyclic trimers **7** may be accounted for by a sequence depicted as follows (Scheme 6). The *2H*-1,2,3-diazaphospholes **3** react with 9-diazofluorene **4a** by a 1,3-dipolar manner. The resultant cycloadducts I decompose with loss of nitrogen to give novel heterocyclic products III containing a three-coordinate pentavalent P atom, which resemble a Staudinger product in character [3]. Thus, trimerization of III provided the oligomeric cyclophosphines **7**.

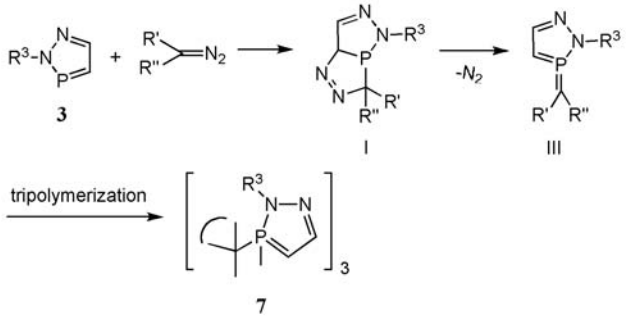
Scheme 5



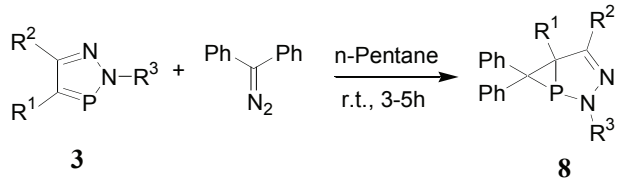
Trimers **6**	R^1	R^2	R^3	R^4	Yields (%)
a	H	Me	H	H	95
b	H	Ph	H	H	88
c	H	*t*-Bu	H	H	56
d		$-(CH_2)_3-$	H	H	79
e	H	Ph	Br	Br	91

Finally, we examined the reactivity of diazaphospholes with diphenyldiazomethane as the 1,3-dipolar component. In a similar manner, the reaction proceeded smoothly under comparable conditions, giving out exclusively the phosphadiazabicyclohexenes **8** by elimination of nitrogen from the initial [2+3]-cycloaddition products in 28-68% yields (Scheme 7).

Scheme 6



Scheme 7



8	R^1	R^2	R^3	m.p. (°C)	Yields (%)
a	H	Me	$COCH_3$	132-135	68
b	H	Ph	$COCH_3$	128-132	66
c	H	*t*-Bu	$COCH_3$	138-140	32
d		$-(CH_2)_3-$	$COCH_3$	124-127	64
e	H	Me	$CO_2C_2H_5$	78-80	50
f	H	Ph	$CO_2C_2H_5$	40-42	52
g	H	*t*-Bu	$CO_2C_2H_5$	99-100	28
h		$-(CH_2)_3-$	$CO_2C_2H_5$	93-95	46

The structures suggested for all the prepared products have been verified by analysis of their analytical and spectroscopic data, which are given in the experimental part. It is well known that the ^{31}P NMR chemical shifts can be affected by many factors such as ring members adjacent to P atom, the anellated ring size, anellation pattern, and additional heteroatoms in the ring [18]. For each of the products **5** and also **8** a highly shielded ^{31}P NMR absorption at δ -92 ~ -45 ppm can be observed, the range compatible with three-coordinate trivalent P atoms [19]. In contrast, the precursors **3** give each a highly deshielded ^{31}P NMR signal at 220-240 ppm. Similar observations are made for the ^{13}C NMR spectra. Thus, the ^{13}C NMR signals found in the range of 42-77 ppm with $^1J_{PC}$ = 127~183 Hz are attributed to the sp^3 hybridized carbon atom in the 3,4-dihydro-*2H*-1,2,3-diazaphophole ring of compounds **5** and **8**. This demonstrated clearly that the original >C=P- bond in **3** has been saturated after reaction. On the other hand, the ^{13}C NMR signal for the sp^2 hybridized carbon atom in the 3,4-dihydro-*2H*-1,2,3-diazaphophole ring of the products remains nearly unchanged, a result in expectation. In addition, the –P=CH in the substrates **3** give each a doublet ^1H NMR signal at 7.8-8.4 ppm with $^2J_{PH}$ 42-44 Hz. In the products **5** and also **8**, the respective >P-CH signal shifted upfield by 4~4.5 ppm, appearing at 3.2~4.5 ppm with $^2J_{PH}$ 20-22 Hz.

On the other hand, the ^{31}P NMR signal for **6** was found at –90.4 ppm, locating in the same range as **5** and **8**. In the ^1H NMR spectrum of cycloadduct **6**, the somewhat upfield doublet at δ 3.15 ppm with $^2J_{PH}$ 21.0 Hz can be assigned to C(7a)-H, whilst the respective signal for –P=CH in the precursor **3c** gives a doublet at δ 8.03 ppm ($^2J_{PH} \approx 43$ Hz).

For the cyclic trimer compounds **7**, the structures have been principally ascertained by NMR and IR spectra along with microelemental analysis. The ^{31}P

NMR signal was at approximately 50 ppm, a range characteristic for three-coordinated P [18]. Furthermore, each of the trimers show a HRMALDI MASS ion peak formed by loss of three acetyl residues.

In conclusion, the present work describes the systematic study on the dipolar cycloaddition reaction between *2H*-1,2,3-diazaphospholes **3** and 9-diazofluorenes **4** or diphenyldiazomethane. Depending on the reaction conditions employed, the corresponding bicyclic phosphiranes **5** and **8** or trimers **7** could be furnished in satisfactory yields. For **3c**, the phosphatetraazabicyclooctadiene **6** has been isolated with no loss of nitrogen.

EXPERIMENTAL

The melting points are uncorrected. Solvents were dried by standard methods. The IR spectra were recorded on a Mattson Alpha-centauri FT-IR spectrometer, using KBr discs. The absorptions are given in wavenumbers (cm^{-1}). ^1H and ^{13}C NMR spectra were acquired in DMSO-d_6, or $CDCl_3$ as solvents on a Bruker 500 or Varian 400 spectrometer with TMS as internal reference. For ^{31}P NMR spectra 85% H_3PO_4 was used as the external reference. Coupling constant (*J*) values are given in Hz. The mass spectra were performed at 70 eV on a Finnigan MAT spectrometer provided with a data system. Satisfactory microanalysis (C±0.20, H±0.20, N±0.30) was obtained for new compounds. All the reactions were carried out under a N_2 atmosphere with strict exclusion of moisture using oven-dried apparatus and glassware. Details for preparation of 2*H*-1,2,3-diazapholspholes **3** have been described elsewhere [20].

Synthesis of the Heterocycles **5** and **8**.

A cyclohexane solution of **3** (10 mmole) is added dropwise to a solution of 9-diazofluorene (1.92 g, 10 mmole) in cyclohexane under stirring at 20 °C, and the resulting mixture is stirred for additional 3~6 hours. The red color faded to yellow over about 2 h, the precipitates are collected by filtration and washed with ether for three times through a porous plate. The product is dried in vacuum to afford the pure **5** or **8** in 28-90% yields.

2-Acetyl-4-methyl-spiro[2,3-diaza-1-phospha]bicyclo[3.1.0]hex-3-ene-6,9'-[9*H*]fluorene (**5a**).

This compound was obtained as yellow powders in 77% yield. M.p. 164-166 °C; ^1H NMR ($CDCl_3$/TMS) δ: 2.26 (s, 3H, CH_3), 2.47 (s, 3H, $COCH_3$), 4.01 (d, 1H, $^2J_{P,H}$ = 21.0, P-CH), 6.74-7.89 (m, $8H_{arom}$); ^{31}P NMR ($CDCl_3$) δ: -75.44; ^{13}C NMR ($CDCl_3$/TMS) δ: 18.65 (CH_3), 21.94 ($COCH_3$), 30.20 (d, $^1J_{C,P}$ =200, C_6), 48.11 (d, $^1J_{C,P}$ = 163.5, C_5), 118.36-145.28 (m, C_{arom}), 157.03 (C_4), 175.16 (d, $^2J_{c,p}$ = 44.5, C=O); IR (KBr) ν (cm^{-1}): 1607 (C=N), 1672 (C=O); MS m/z (%): 306 (M^+, 69), 264 (100), 263 (91); HRMS calcd for $C_{18}H_{15}N_2OP$ 306.0922, found 306.0932.

2-Acetyl-4-phenyl-spiro[2,3-diaza-1-phospha]bicyclo[3.1.0]hex-3-ene-6,9'-[9*H*]fluorene (**5b**).

This compound was obtained as pale-yellow powders in 90% yield. M.p. 160-161°C; ^1H NMR ($CDCl_3$/TMS) δ: 2.60 (s, 3H, $COCH_3$), 4.53 (d, 1H, $^2J_{P,H}$ = 20.2, P-CH), 7.12-7.95 (m, $13H_{arom}$); ^{31}P NMR ($CDCl_3$) δ: -63.66; ^{13}C NMR ($CDCl_3$/TMS) δ: 21.94 ($COCH_3$), 33.04 (d, $^1J_{c,p}$ = 198.7, C_6), 49.65 (d, $^1J_{c,p}$ = 164.2, C_5), 120.13-141.44 (m, C_{arom}), 156.80 (C_4), 177.36 (d, $^2J_{c,p}$ = 44.6, C=O); IR (KBr) ν (cm^{-1}): 1618 (C=N), 1665 (C=O); MS m/z (%): 368 (M^+, 23), 165 (100), 133 (85); HRMS calcd for $C_{23}H_{17}N_2OP$ 368.1079, found 368.1065.

17-Acetyl-17,18-diaza-16-phosphaspiro[fluorene-9,2'-tricyclo-[4.3.0.0^{1,3}]nonane]-18-ene (**5c**).

This compound was obtained as pale-yellow powders in 83% yield. M.p. 134-136 °C; ^1H NMR ($CDCl_3$/TMS) δ: 2.07-2.21 (m, 4H, $2CH_2$), 2.46 (s, 3H, $COCH_3$), 2.60 (t, 2H, C_3-H_2), 6.89-7.84 (m, $8H_{arom}$); ^{31}P NMR ($CDCl_3$) δ: -45.16; ^{13}C NMR ($CDCl_3$/TMS) δ: 22.67 ($COCH_3$), 22.74, 26.92, 27.88 (CH_2), 36.41 (d, $J_{c,p}$ = 197.0, C_{13}), 61.94 (d, $^1J_{c,p}$ = 183.5, C_{14}), 120.11-142.99 (m, C_{arom}), 168.81 (C_{19}), 175.47 (d, $^2J_{c,p}$ = 44.5, C=O); IR (KBr) ν (cm^{-1}): 1630 (C=N), 1672 (C=O); MS m/z (%):332 (M^+, 62), 43 (100), 289 (44); HRMS calcd for $C_{20}H_{17}N_2OP$ 332.1453, found 332.1436.

2-Acetyl-4-phenyl-spiro[2,3-diaza-1-phospha]bicyclo[3.1.0]hex-3-ene-6,9'-[9*H*]-2',7'-dichlorofluorene (**5d**).

This compound was obtained as pale-yellow powders in 82% yield. M.p. 118-120 °C; ^1H NMR ($CDCl_3$/TMS) δ: 2.28 (s, 3H, $COCH_3$), 3.65 (d, 1H, $^2J_{P,H}$ = 20.3, P-CH), 7.28-7.96 (m, $11H_{arom}$); ^{31}P NMR ($CDCl_3$) δ: -68.32; ^{13}C NMR ($CDCl_3$/TMS) δ: 22.25 ($COCH_3$), 32.81 (d, $^1J_{C,P}$ = 190.5, C_6), 46.99 (d, $^1J_{C,P}$ = 162.5, C_5), 119.04-142.86 (m, C_{arom}), 156.36 (C_4), 172.30 (d, $^2J_{C,P}$ = 44.2, C=O); IR (KBr) ν (cm^{-1}): 1625 (C=N), 1690 (C=O); MS m/z (%): 436 (M^+, 18), 103 (100), 196 (90); HRMS calcd for $C_{23}H_{15}Cl_2N_2OP$ 436.0300, found 436.0321.

2-Acetyl-4-phenyl-spiro[2,3-diaza-1-phospha]bicyclo[3.1.0]hex-3-ene-6,9'-[9*H*]-2',7'-dibromofluorene (**5e**).

This compound was obtained as yellow powders in 89% yield. M.p. 124-126 °C; ^1H NMR ($CDCl_3$/TMS) δ: 2.01 (s, 3H, $COCH_3$), 3.62 (d, 1H, $^2J_{P,H}$ = 20.4, P-CH), 7.38-7.76 (m, $11H_{arom}$); ^{31}P NMR ($CDCl_3$) δ: -70.56; ^{13}C NMR ($CDCl_3$/TMS) δ: 22.96 ($COCH_3$), 35.22 (d, $^1J_{C,P}$ = 199.2, C_6), 48.23 (d, $^1J_{C,P}$ = 163.7, C_5), 121.36-145.22 (m, C_{arom}), 154.66 (C_4), 176.36 (d, $^2J_{C,P}$ = 44.2, C=O); IR (KBr) ν (cm^{-1}): 1621 (C=N), 1682 (C=O); MS m/z (%): 526 (M^+, 20), 163 (100), 243 (61); HRMS calcd for $C_{23}H_{15}Br_2N_2OP$ 523.9289, found 523.9272.

5-Acetyl-5,7a-dihydro-7-(tert-butyl)-spiro[3H-1,2,4-diazaphospholo][4,3-*c*][1,2,3]diazaphosphole-3,9'-[9*H*]fluorene (**6**).

This compound was obtained as gray powders in 65% yield. M.p. 118-120 °C; ^1H NMR ($CDCl_3$/TMS) δ: 1.11 (s, 9H, $C(CH_3)_3$), 2.34 (s, 3H, $COCH_3$), 3.15 (d, 1H, $^2J_{P,H}$ = 21.0, P-CH), 7.21-7.68 (m, $8H_{arom}$); ^{31}P NMR ($CDCl_3$) δ: -90.35; ^{13}C NMR ($CDCl_3$/TMS) δ: 21.87 ($COCH_3$), 28.30 ($C(CH_3)_3$), 34.6 ($C(CH_3)_3$), 36.25 (d, $^1J_{c,p}$ = 188.2, C_3), 46.50 (d, $^1J_{c,p}$ = 163.0, C_{7a}), 118.82-142.89 (m, C_{arom}), 158.62 (C_7), 172.08 (d, $^2J_{c,p}$ = 44.5, C=O); IR (KBr) ν (cm^{-1}): 1560 (N=N), 1630 (C=N), 1700 (C=O); MS m/z (%): 319 (M^+- $C(CH_3)_3$, 4),165 (100), 261 (29), 318 (M^++1-$C(CH_3)_3$, 13); HRMS calcd for $C_{21}H_{21}N_4OP$-C_4H_9 319.0749, found 319.0739.

Synthesis of the Trimer **7**.

A solution of **3** (5 mmole) and equimolar amount of 9-diazofluorene in dry CH_2Cl_2 (5 mmole) or benzene is stirred at 20 °C for 3~5 hours. The solution turned to a thick suspension upon completion of the reaction. Then, ether or cyclohexane was added, and the yellow precipitates were collected by suction. The yellow colored solids were washed with cold ether and dried at vacuum to give pure **7** in 56-95% yields.

Cyclic Trimer (**7a**).

This compound was obtained as yellow powders in 95% yield. M.p. 256-258 °C; IR (KBr) ν (cm^{-1}): 739 (s), 1228, 1260 (m), 1335 (s), 1611 (w), 1672 (vs).

Anal. Calcd for $C_{54}H_{45}N6_2O_3P_3$ (%): C, 70.57; H, 4.93; N, 9.14. Found: C, 70.38; H, 4.90; N, 9.29.

Cyclic Trimer (**7b**).

This compound was obtained as yellowish brown powders in 88% yield. M.p.186 –188 °C; IR (KBr) ν (cm^{-1}): 739 (s), 1246, 1280 (m), 1347 (s), 1630 (w), 1676 (vs); HRMALDIMS for $C_{69}H_{51}N_6O_3P_3$ (M^++1-3$COCH_3$): calc 976.1868, found 976.1891.

Cyclic Trimer (**7c**).

This compound was obtained as grayish brown powders in 56% yield. M.p.80-82 °C; ^{1}H NMR ($CDCl_3$/TMS) δ: 0.74 (s, 9H, C(CH_3)$_3$), 2.55 (s, 3H, $COCH_3$), 5.43 (d, 1H, $^2J_{P,H}$ = 31.6, P=CH), 7.27-8.09 (m, 8H$_{arom}$); ^{31}P NMR ($CDCl_3$) δ: 51.88; ^{13}C NMR ($CDCl_3$) δ: 21.86 (CO*C*H$_3$), 27.04 (C(*C*H$_3$)$_3$), 29.00 (*C*(CH$_3$)$_3$), 36.36 (d, $^1J_{C,P}$ = 187.0, C-P), 120.42-143.82 (m, C$_{arom}$), 138.70 (d, $^1J_{C,P}$ =12.0, C=P), 173.38 (d, $^2J_{C,P}$ = 43.6, C=O); IR (KBr) ν (cm^{-1}): 741 (s), 1244, 1283 (m), 1350 (s), 1637 (w), 1677 (vs); HRMALDIMS for $C_{63}H_{63}N_6O_3P_3$ (M^++1-3$COCH_3$): calc 916.2807, found 916.2787.

Cyclic Trimer (**7d**).

This compound was obtained as yellow powders in 79% yield. M.p.90-92 °C; IR (KBr) ν (cm^{-1}): 746 (s), 1235, 1266 (m), 1375 (s), 1621 (w), 1665 (vs); HRMALDIMS for $C_{60}H_{51}N_6O_3P_3$ (M^++1-3$COCH_3$): calc 868.1868, found 868.1890.

Cyclic Trimer (**7e**).

This compound was obtained as yellow powders in 91% yield. M.p.163-165 °C; ^{1}H NMR ($CDCl_3$/TMS) δ: 2.69 (s, 3H, $COCH_3$), 5.50 (d, 1H, $^2J_{P,H}$ = 32.3, P=CH), 7.30-7.68 (m, 8H$_{arom}$); ^{31}P NMR ($CDCl_3$) δ: 48.76; ^{13}C NMR ($CDCl_3$/TMS) δ: 22.45 (CO*C*H$_3$), 35.81 (d, $^1J_{C,P}$ = 199.0, C-P), 120.44-146.32 (m, C$_{arom}$), 140.75 (d, $^1J_{C,P}$ = 12.0, C=P), 175.34 (d, $^2J_{C,P}$ = 43.4, C=O); IR (KBr) ν (cm^{-1}): 741 (s), 1236, 1270 (m), 1342 (s), 1625 (w), 1690 (vs); HRMALDIMS for $C_{69}H_{45}Br_6N_6O_3P_3$ (M^++1-3$COCH_3$): calc 1443.6498, found 1443.6517.

Synthesis of the Heterocycles (**8**).

These compounds were prepared as described as for compounds **5** by using diphenyldiazomethane in place of 9-diazofluorene.

2-Acetyl-4-methyl-6,6-diphenyl-2,3-diaza-1-phosphabicyclo-[3.1.0]hex-3-ene (**8a**).

This compound was obtained as white powders in 68% yield. M.p. 132-135 °C. ^{1}H NMR ($CDCl_3$/TMS) δ: 2.00 (s, 3H, CH_3), 2.20 (s, 3H, $COCH_3$), 3.76 (d, 1H, $^2J_{P,H}$ = 20.2, P-CH), 6.84-7.35 (m, 10H$_{arom}$); ^{31}P NMR ($CDCl_3$) δ: -92.82; ^{13}C NMR ($CDCl_3$/TMS) δ: 19.27 (CH_3), 21.55 (CO*C*H$_3$), 38.44 (d, $^1J_{c,p}$ = 189.0, C$_6$), 50.40 (d, $^1J_{c,p}$ = 145.5, C$_5$), 126.15-142.42 (m, C$_{arom}$), 157.28 (C$_4$), 174.99 (d, $^2J_{c,p}$ = 41.0, C=O); IR (KBr) ν (cm^{-1}): 1602 (C=N), 1657 (C=O); MS m/z (%): 308 (M^+, 25), 165 (100), 265 (42); HRMS calcd for $C_{18}H_{17}N_2OP$ 308.1079, found 308.1062.

2-Acetyl-4,6,6-triphenyl-2,3-diaza-1-phosphabicyclo[3.1.0]hex-3-ene (**8b**).

This compound was obtained as white powders in 66% yield. M.p. 128-132 °C. ^{1}H NMR ($CDCl_3$/TMS) δ: 2.12 (s, 3H, $COCH_3$), 4.29 (d, 1H, $^2J_{P,H}$ = 19.7, P-CH), 6.97-7.88 (m, 15H$_{arom}$); ^{31}P NMR ($CDCl_3$) δ: -90.50; ^{13}C NMR ($CDCl_3$/TMS) δ: 21.55 (CO*C*H$_3$), 39.03 (d, $J_{c,p}$ = 187.0, C$_6$), 47.02 (d, $^1J_{c,p}$ = 144.0, C$_5$), 126.44-142.48 (m, C$_{arom}$), 156.32 (C$_4$), 175.40 (d, $^2J_{c,p}$ = 39.5, C=O); IR (KBr) ν (cm^{-1}): 1594 (C=N), 1668 (C=O); MS m/z (%): 370 (M^+, 24), 165 (100), 327 (41); HRMS calcd for $C_{23}H_{19}N_2OP$ 370.1235, found 370.1224.

2-Acetyl-4-(tert-buty)l-6,6-diphenyl-2,3-diaza-1-phosphabicyclo-[3.1.0]hex-3-ene (**8c**).

This compound was obtained as white powders in 32% yield. M.p. 138-140 °C. ^{1}H NMR ($CDCl_3$/TMS) δ: 1.29 (s, 9H, C(CH_3)$_3$), 2.03 (s, 3H, $COCH_3$), 3.98 (d, 1H, $^2J_{P,H}$ = 19.4, P-CH), 6.97-7.34 (m, 10H$_{arom}$); ^{31}P NMR ($CDCl_3$) δ: -88.69; ^{13}C NMR ($CDCl_3$/TMS) δ: 21.53 (CO*C*H$_3$), 29.09 (C(*C*H$_3$)$_3$), 35.92 (*C*(CH$_3$)$_3$), 38.75 (d, $^1J_{c,p}$ = 184.5, C$_6$), 47.98 (d, $^1J_{c,p}$ = 141.5, C$_5$), 126.52-142.52 (m, C$_{arom}$), 166.30 (C$_4$), 175.43 (d, $^2J_{c,p}$ = 41.5, C=O); IR(KBr) ν (cm^{-1}): 1610 (C=N), 1690 (C=O); MS m/z (%): 350 (M^+, 24), 165 (100), 307 (10); HRMS calcd for $C_{21}H_{23}N_2OP$ 350.1548, found 350.1533.

4-Acetyl-4,5-diaza-2,2-diphenyl-3-phospha-tricyclo[4.3.0.0^{1,3}]-non-5-ene (**8d**).

This compound was obtained as white powders in 64% yield; M.p. 124-127 °C. ^{1}H NMR ($CDCl_3$/TMS) δ: 1.97 (s, 3H, $COCH_3$), 2.09-2.69 (m, 6H, 3CH_2), 6.78-7.34 (m, 10H$_{arom}$); ^{31}P NMR ($CDCl_3$) NMR δ: -64.92; ^{13}C ($CDCl_3$/TMS) δ: 21.67 (CO*C*H$_3$), 25.00, 27.65, 28.31 (CH_2), 42.58 (d, $^1J_{c,p}$ =167.5, C$_2$), 64.66 (d, $^1J_{C,P}$ = 164.5, C$_1$), 126.11-140.71 (m, C$_{arom}$), 169.62 (C$_6$), 175.12 (d, $^2J_{C,P}$ = 39.5, C=O); IR (KBr) ν (cm^{-1}): 1622 (C=N), 1670 (C=O); MS m/z (%): 334 (M^+, 50), 165 (100), 215 (70); HRMS calcd for $C_{20}H_{19}N_2OP$ 334.1235, found 334.1249.

2-Ethoxycarbonyl-4-methyl-6,6-diphenyl-2,3-diaza-1-phospha-bicyclo[3.1.0]hex-3-ene (**8e**).

This compound was obtained as white powders in 50% yield. M.p. 78-80 °C. ^{1}H NMR ($CDCl_3$/TMS) δ: 1.28 (t, 3H, *J*= 7.0, OCH_2CH_3), 2.24 (s, CH_3), 3.80 (d, 1H, $^2J_{P,H}$ = 18.4, P-CH), 4.24 (q, 2H, *J* = 7.0, OCH_2CH_3), 7.14-7.80 (m, 10H$_{arom}$); ^{31}P NMR ($CDCl_3$) δ: -86.68; ^{13}C NMR ($CDCl_3$/TMS) δ: 14.35 (OCH_2CH_3), 18.76 (CH_3), 37.26 (d, $^1J_{c,p}$ = 188.2, C$_6$), 48.68 (d, $^1J_{c,p}$ = 143.5, C$_5$), 62.56 (OCH_2CH_3), 127.47-142.99 (m, C$_{arom}$), 158.76 (C$_4$), 172.03 (d, $^2J_{c,p}$ = 42.0, C=O); IR (KBr) ν (cm^{-1}): 1598 (C=N), 1695 (C=O); MS m/z (%): 338 (M^+, 23), 165 (100), 265 (39); HRMS calcd for $C_{19}H_{19}N_2O_2P$ 338.1184, found 338.1199.

2-Ethoxycarbonyl-4,6,6-triphenyl-2,3-diaza-1-phosphabicyclo-[3.1.0]hex-3-ene (**8f**).

This compound was obtained as white solids in 52% yield. M.p. 40-42 °C. ^{1}H NMR ($CDCl_3$/TMS) δ: 1.24 (t, 3H, J = 7.1, OCH_2CH_3), 3.22 (d, 1H, $^2J_{P,H}$ = 7.9, P-CH), 4.32 (q, 2H, J = 7.1, OCH_2CH_3), 6.93-7.44 (m, 15H_{arom}); ^{31}P NMR ($CDCl_3$) δ: -85.05; ^{13}C NMR ($CDCl_3$/TMS) δ: 14.36 (OCH_2CH_3), 32.60 (d, $^1J_{c,p}$ = 183.5, C_6), 45.80 (d, $^1J_{c,p}$=142.0, C_5), 62.81 (OCH_2CH_3), 126.31-148.36 (m, C_{arom}), 156.21 (C_4), 168.08 (d, $^2J_{c,p}$ = 43.0, C=O); IR (KBr) ν (cm^{-1}): 1608 (C=N), 1702 (C=O); MS m/z (%): 400 (M^+, 10), 165 (100), 77 (98); HRMS calcd for $C_{24}H_{21}N_2O_2P$ 400.1341, found 400.1352.

2-Ethoxycarbonyl-4-(*tert*-butyl)-6,6-diphenyl-2,3-diaza-1-phosphabicyclo[3.1.0]hex-3-ene (**8g**).

This compound was obtained as white solids in 28% yield. M.p. 99-100 °C. ^{1}H NMR ($CDCl_3$/TMS) δ: 1.31 (s, 9H, $C(CH_3)_3$), 1.47 (t, 3H, J = 7.1, OCH_2CH_3), 4.05 (d, 1H, $^2J_{P,H}$ = 17.6, P-CH), 4.28 (q, 2H, J = 7.1, OCH_2CH_3), 7.21-7.34 (m, 10H_{arom}); ^{31}P NMR ($CDCl_3$) δ: -82.64; ^{13}C NMR ($CDCl_3$/TMS) δ: 14.60 (OCH_2CH_3), 29.14 [$(CH_3)_3C$], 36.03 [$(CH_3)_3C$], 40.27 (d, $^1J_{c,p}$ = 187.0, C_6), 49.80 (d, $^1J_{c,p}$ = 141.8, C_5), 63.00 (OCH_2CH_3), 126.34-142.82 (m, C_{arom}), 157.08 (C_4), 166.14 (d, $^2J_{c,p}$ = 42.5, C=O); IR (KBr) ν (cm^{-1}): 1603 (C=N), 1686 (C=O); MS m/z (%): 380 (M^+, 15), 165 (100), 178 (10); HRMS calcd for $C_{22}H_{25}N_2O_2P$ 380.1655, found 380.1636.

4-Ethoxylcarbonyl-4,5-diaza-2,2-diphenyl-3-phospha-tricyclo-[4.3.0.0^{1,3}]non-5-ene (**8h**).

This compound was obtained as white solids in 46% yield. M.p. 93-95 °C. ^{1}H NMR ($CDCl_3$/TMS) δ: 1.46 (t, 3H, J = 7.1, OCH_2CH_3), 2.10-3.10 (m, 6H, $3CH_2$), 4.25 (q, 2H, J = 7.1, OCH_2CH_3), 6.75-7.33 (m, 10H_{arom}); ^{31}P NMR ($CDCl_3$) δ: -58.32; ^{13}C NMR ($CDCl_3$/TMS) δ: 14.60 (OCH_2CH_3), 23.41, 24.83, 27.77 (CH_2), 45.89 (d, $^1J_{c,p}$ = 164.5, C_2), 60.89 (d, $^1J_{c,p}$ = 162.7, C_1), 62.89 (OCH_2CH_3), 125.98-138.19 (m, C_{arom}), 158.88 (C_6), 169.03 (d, $^2J_{c,p}$ = 40.5, C=O); IR (KBr) ν (cm^{-1}): 1625 (C=N), 1706 (C=O); MS m/z (%): 364 (M^+, 25), 165 (100), 283 (52); HRMS calcd for $C_{21}H_{21}N_2O_2P$ 364.1341, found 364.1359.

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