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Chemistry of phosphorus ylides. Part 24 [1]. A route for the synthesis of oxazine derivatives *via* the reaction of phosphacumulenes and phosphallene with di- and tri-ketone monoximes

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Abstract The reaction of bifunctional di- and tri-ketone monoximes with (*N*-phenylimino-vinylidene)-, (oxovinylidene)-, and (thioxovinylidene)-triphenylphosphorane was performed. These phosphacumulene ylides react with the oxime OH group rather than the carbonyl group by addition to give the corresponding phosphoranylidenes. Some of these phosphoranylidenes cyclized according to an intramolecular *Wittig* reaction to give the oxazines along with triphenylphosphine oxide. On the other hand, the monoximes afforded only the phosphoranylidenes when they were allowed to react with the hexaphenylcarbodiphosphorane. The reaction course between the phosphacumulenes and phosphallene with monoximes was found to depend on the nature of the reactants.

Keywords Phosphacumulenes; Phosphallene; Ketone monoxime derivatives; Phosphoranylidenes; Oxazines.

Introduction

By virtue of their enhanced reactivity and the versatility of their nucleophilic reactions, the phosphacumulene ylides **1a**–**1c**, are potentially useful synthons as reagents recently used for the synthesis of heterocycles [1, 2]. As part of our interest in these phosphorus reagents [1], we describe here their behavior towards 1,2-diphenylethane-1,2-dione monoxime (**3**), phenanthrene-9,10-dione monoxime (**7**), 1-methyl-1*H*-indole-2,3-dione-3-oxime (**11**), and indan-1,2,3-trione-2-oxime (**14**) and compare their reactivity with that of the phosphallene ylide **2** towards the above mentioned monoximes. Products of these reactions are of expected synthetic, pharmacological, and industrial utility [3].

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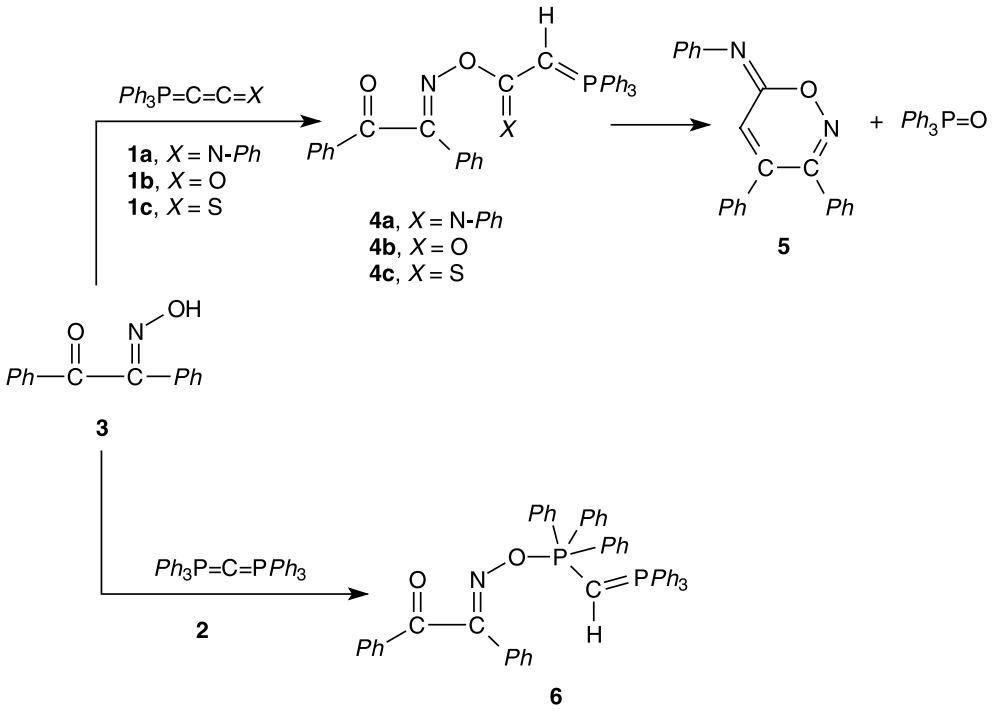
Results and discussion

When **3** was treated with equimolar amount of (*N*-phenyliminovinylidene)triphenylphosphorane (**1a**), in *THF* at 25°C for 10 h, (3,4-diphenyl[1,2]oxazin-6-ylidene)phenylamine (**5**) was obtained in good yield, together with triphenylphosphine oxide. Addition of **3** to **1a**, afforded the reactive intermediate phosphorane **4a**, which cyclizes according to an intramolecular *Wittig* reaction yielding the corresponding oxazinylidene **5** (Scheme 1). The IR spectrum of **5** revealed the absence of =N–OH and C=O bands, which appeared in the starting material **3** at $\bar{\nu} = 3392$ and 1644 cm^{-1}. The ^1H NMR spectrum of **5** exhibits signals at $\delta = 4.42$ (CH) and 7.58–7.88 (15H-aromatic) ppm whereas its ^{13}C NMR spectrum revealed the absence of carbonyl group and the presence of a C=N group at $\delta = 162.03$ ppm.

When the reaction of **3** with (2-oxovinylidene)-(**1b**), and (2-thioxovinylidene)-triphenylphospho-



Scheme 1

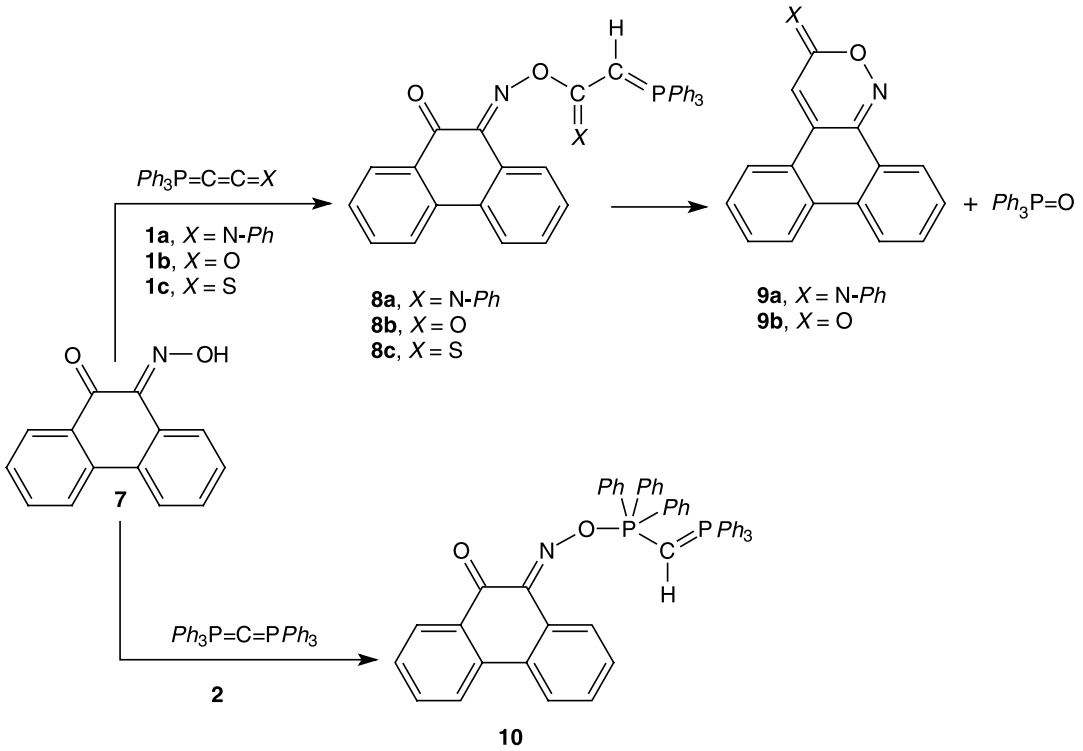
rane (**1c**) was performed in boiling toluene the corresponding 1,2-diphenylethane-1,2-dione-*O*-[2-(triphenylphosphoranylidene)acetyl]oxime (**4b**) and 1,2-diphenylethane-1,2-dione-*O*-[2-(triphenylphosphoranylidene)ethanethioyl]oxime (**4c**) were obtained. The IR spectrum of **4b** confirms the proposed structure showing no absorption band for the =N–OH group. The ester and the aryl carbonyls appeared at $\bar{\nu} = 1729$ and 1665 cm^{-1}. Its ^1H NMR spectrum displayed signals at $\delta = 5.05$ (d, 1H, $^2J_{HP} = 27$ Hz, CH=P) and 7.54–7.74 (25H-aromatic) ppm. The ^{31}P NMR shift recorded for **4b** was $\delta = 29.1$ ppm.

Furthermore, the reaction of **3** with the phosphallene ylide, namely, hexaphenylcarbodiphosphorane (**2**) was investigated. Compounds **2** and **3** react in equimolar ratio in *THF*, to give 1,2-diphenylethane-1,2-dione-*O*-{triphenyl[2-triphenylphosphoranylidene)methyl]phosphoranyl}-oxime (**6**). The structure of **6** is corroborated by the frequency of the C=O band in the IR spectrum at $\bar{\nu} = 1619\ cm^{-1}$ and the absence of the =N–OH group. The ^1H NMR spectrum of **6** shows signals at $\delta = 5.61$ (dd, 1H, $^2J_{1,2HP} = 27$, 33 Hz, P–CH=P), and 7.27–7.65 (40H-aromat) ppm. The ^{31}P NMR shifts of **6** were δ 24.36 (P=C) [4], and 20.33 (O–P). Upon heating adduct **6** in boiling toluene for 8 h, it was recovered unchanged.

In addition, the behavior of phenanthrene-9,10-dione monoxime (**7**) towards the phosphacumulene ylide **1a** was studied. When **7** was treated with **1a**, in *THF* in the cold for 8 h, (2-oxa-1-azatriphenylene-3-ylidene)phenylamine (**9a**), was obtained directly along with triphenylphosphine oxide, and the intermediate phosphoranylidene **8a** was not isolated. Structural assignment for **9a** was supported by the MS, IR, and the ^1H NMR spectroscopic data. The IR is characterized by the absence of =N–OH and C=O groups. The ^1H NMR spectrum revealed the presence of the oxazine proton at $\delta = 4.14$ (CH) and the aromatic protons at 7.07–7.70 ppm.

The reaction of **7** with **1b** and **1c** was performed in boiling toluene for 8 h in case of **1b** and 12 h in case of **1c**, to give the corresponding phosphoranylidenes **8b** and **8c**. When the phosphor- anylidene **8b** was heated in a cold finger sublimator at 130°C for 30 min under reduced pressure (0.5 mm Hg), 2-oxa-1-aza-triphenylen-3-one (**9b**) together with triphenylphosphine oxide were produced. Adduct **8c** was recovered unchanged upon heating in toluene for 3 h or thermolysis under reduced pressure.

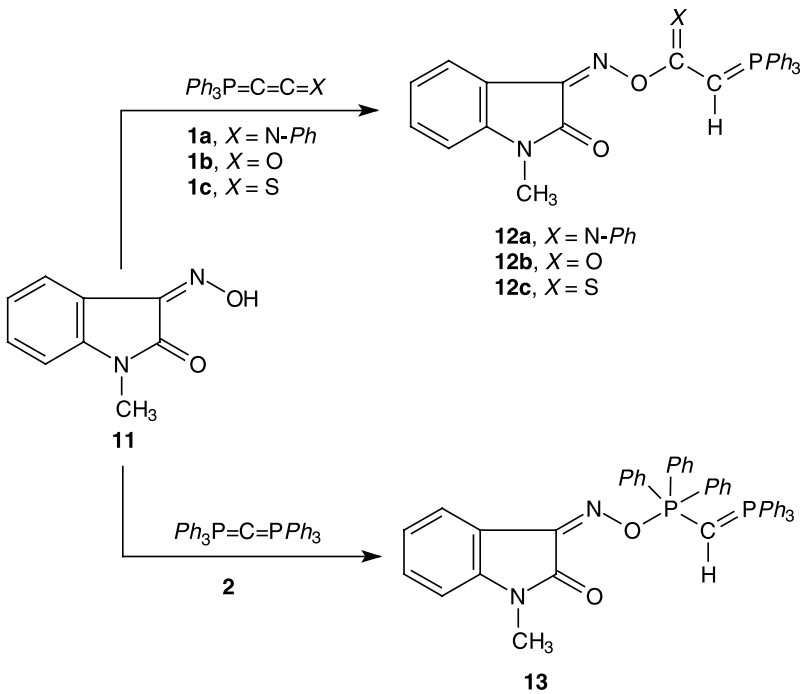
Treatment of **7** with **2** in *THF* solution at room temperature afforded phenanthrene-9,10-dione-*O*-{triphenyl[(triphenylphosphoranylidene)methyl]-phosphoranyl}oxime (**10**). Repetition of the reaction



Scheme 2

in boiling toluene afforded the same product **10**. The elemental analyses and spectroscopic data exclude any cycloaddition reaction (Scheme 2).

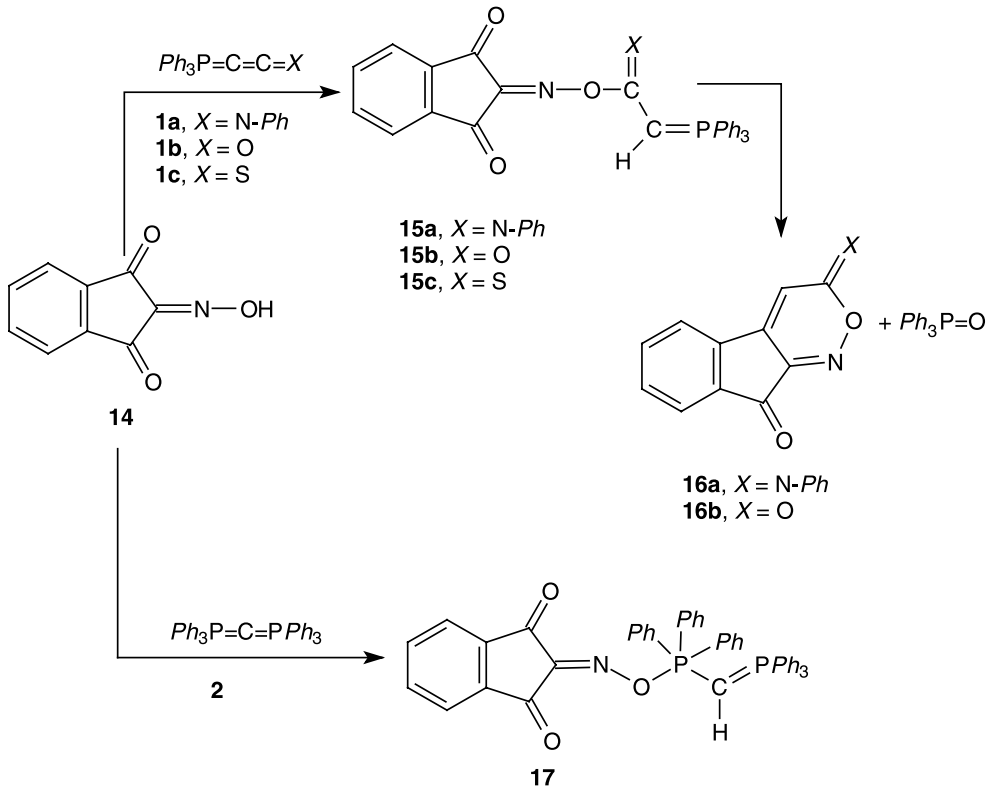
Isatin *O*-acyl oximes selectively, inhibit Ubiquitin C-terminal hydrolase (UCH-L_1), which is responsible for progression of nonneuronal tumors as certain



Scheme 3

lung tumor [5]. Therefore, we studied the reaction of 1-methyl-1*H*-indole-2,3-dione-3-oxime (**11**), with the phosphacumulenes **1a**–**1c** and the phosphallene **2** to prepare new indole derivatives for pharmacological evaluation as inhibitors of UCH-L_1 (Scheme 3). The reactions proceeded in *THF* at room temperature for 6 h in case of **12a**, **12b** and 8 h in case of **12c** and **13**. In all cases the reactions proceeded by addition of the monoxime **11** to the phosphonium ylides **1a**–**1c** and **2**, with the formation of phosphoranylidenes **12a**–**12c** and **13**. The structures of **12a**–**12c** and **13** were supported with the elemental analyses and spectroscopic data. The IR spectrum of 1-methyl-*H*-indole-2,3-dione-3-{*O*-[*N*-phenyl-2-(triphenylphosphoranylidene)ethanimidoyl]oxime} (**12a**) exhibited the presence of the amide carbonyl at $\bar{\nu} = 1650\,\mathrm{cm}^{-1}$, and the absence of the hydroxyl group. Its ^{1}H NMR spectrum showed the presence of signals at $\delta = 3.33$ (CH_3), 5.41 (d, 2H, $^2J_{HP} = 24$ Hz, CH=P) and 7.7 (24H-aromatic) ppm. The N–*C*H_3, *C*=P, O–C=N–*Ph*, C=N–O and *C*=*O*, in the ^{13}C NMR spectrum appeared at $\delta = 30.47$, 149.45, 152.21, 156.56 and 163.05 ppm. The ^{31}P NMR of **12a** showed one signal at $\delta = 24.35$ ppm and the mass spectrum indicated the presence of ion peaks at $m/z = 524$ (M^+-C=O) and 376 [$(Ph)_3$P=C=C=N–*Ph*], which can originate *via* cleavage of the molecular ion peak at $m/z = 553$.

N-Substituted-1,3-diones have been proven to be potent cytotoxic agents effective against the growth of single cell Leukemia tumors and cell lines derived from solid tumors. Some of the derivatives were active against growth of solid tumors *e.g.*, colon, lung bronchogenic, and asteosarcoma for which a few effective agents are available to inhibit their growth [6]. Therefore, new oxazine and phosphoranylidenes derived from **14**, of pharmacological importance were synthesized. Thus, **14** was reacted with **1a** in *THF* in the cold for 8 h, yielding 3-phenylimino-3*H*-2-oxa-1-aza-fluoren-9-one (**16a**). Its IR spectrum of **16a** showed an absorption band at $\bar{\nu} = 1708\,\mathrm{cm}^{-1}$ attributable to the indanone carbonyl. The ^{1}H NMR shifts of **16a** were $\delta = 4.14$ (CH) and 6.99–7.94 (9H-aromat) ppm. It disclosed the absence of OH group, which appeared in the starting material **14** at $\delta = 14.36$. The ^{13}C NMR of **16a** showed signals at $\delta = 197.28$ (*C*=*O*), 165.41 (C=N–*Ph*), and 146.37 (C=N–O) ppm.



Scheme 4

The reaction of **14** and **1b** was performed in *THF* at room temperature for 10 h, to give 1*H*-indene-1,2,3-trione-2-{*O*-[2-(triphenylphosphoranylidene)-acetyl]oxime} (**15b**). When **14** was heated with **1b** in toluene for 8 h, 2-oxa-1-aza-fluorene-3,9-dione (**16b**) was obtained along with triphenylphosphine oxide. The reaction of **14** with **1c** and **2** was also investigated. When **14** was allowed to react with **1c** and **2** in toluene for 6 and 8 h, the corresponding 1*H*-indene-1,2,3-trione-2-{*O*-[2-(triphenylphosphoranylidene)ethanethioyl]oxime} (**15c**) and/or 1*H*-indene-1,2,3-trione-2-(*O*-{triphenyl[2-(triphenylphosphoranylidene)methyl]phosphoranyl}oxime) (**17**) were obtained in good yield.

Conclusion

The reaction of phosphacumulene ylides **1a**–**1c** with bifunctional di- and tri-ketone monoximes **3**, **7**, **11**, and **14** represents an interesting approach to the construction of new heterocycles. These phosphacumulenes react with the oxime OH group rather than the carbonyl group by addition to give the phosphoranylidenes, **4**, **8**, **12**, and **15**. The difference in the nucleophilic character and reactivity of the phosphacumulenes **1a** > **1b** > **1c** [7], is also demonstrated in this study. Thus **1a** reacted smoothly with the di- and tri-ketone monoximes **3**, **7**, **11**, and **14**, to give the phosphoranylidenes **4a**, **8a**, **12a**, and **15a**, which are readily cyclized according to an intramolecular *Wittig* reaction in the case of **4a**, **8a**, and **15a** to give the corresponding oxazines **5a**, **9a**, and **16a** along with triphenylphosphine oxide. Moreover, **1b** reacted less rapidly to yield the corresponding phosphoranylidenes, **4b**, **8b**, **12b**, and **15b**. Upon heating or thermolysis of the later adducts, compounds **4b** and **12b** were recovered unchanged, while **8b** and **15b** were cyclized to yield the respective oxazinones **9b** and **16b**. On the other hand, the monoximes **3**, **7**, **11**, and **14**, afforded only the phosphoranylidenes **4c**, **8c**, **12c**, **15c**, **6**, **10**, **13**, and **17**, when they were allowed to react with **1c** or the allylic diphosphorane **2**. It has been previously reported [8] that the reaction of the stabilized phosphorus ylides, namely methoxy- and ethoxy-carbonylmethylenetriphenylphosphorane, with quinone monoximes afford the corresponding pyrrole derivatives. Therefore, it is safe to state that the reaction course between the active phosphacumulenes, phosphallene, and stabilized phosphorus ylides with monoximes, is rather dependent on a number of parameters. These include the nature of the reactants, type of the solvent and the reaction temperature. This process can be considered as a simple route for the formation of oxazinone derivatives and their thioanalogues.

Experimental

All melting points were measured on a *Gallenkamp* electrothermal melting point apparatus. The infrared spectra were recorded in *KBr* pellets on *Pye* unicam SP 3300 and FTIR 8101PC *Shimadzu* Infrared Spectrometers. NMR spectra were obtained in $CDCl_3$ or *DMSO*-d_6 on a Varian MERCURY (^{1}H: 300 MHz, ^{13}C: 75 MHz) spectrometer using *TMS* as an internal reference. ^{31}P NMR spectra were run on the same spectrometer using, H_3PO_4 (85%) as an external reference. Mass spectra were recorded on a *Shimadzu* GC-MS QP 1000 Ex Spectrometer at (E I, 70 eV). Elemental analyses were carried out at Microanalytical center of National Research Center, El-Tahrir Street, Dokki, Cairo. Their results were in agreement with the calculated values.

(3,4-Diphenyl-[1,2]oxazin-6-ylidene)phenylamine (**5**, $C_{22}H_{16}N_2O$)
A solution of 377 mg **1a** [9] (1 mmol) in 20 cm^3 *THF* was added dropwise with stirring to a solution of 225 mg **3** [10] (1 mmol) in 20 cm^3 *THF*. The reaction mixture was kept for 10 h at room temperature during which the color changed from white to pale brown. The solvent was removed under reduced pressure and the residue was chromatographed on silica gel using pet. ether (60–80°C):ethyl acetate as eluent (9:1, *v*/*v*) to give 160 mg **5** (50%) and 100 mg triphenylphosphine oxide (35%), MS (EI): $m/e = 324$.

*Reaction of 1,2-diphenylethane-1,2-dione momoxime (**3**), with (2-oxovinylidene)- (**1b**)- and (2-thioxovinylidene)-triphenylphosphorane (**1c**). Preparation of the phosphoranylidenes **4b** and **4c***
A mixture of 302 mg **1b** or 319 mg **1c** [11] (1 mmol), 225 mg of **3** (1 mmol), and 40 cm^3 toluene was refluxed for 10 h in case of **1b** and 15 h in case of **1c**. Toluene was removed under reduced pressure and the residue was subjected to silica gel column chromatography using pet. ether (60–80°C):acetone (8:2, *v*/*v*) as an eluent to give **4b** and **4c**.

1,2-Diphenylethane-1,2-dione-O-[2-(triphenylphosphoranylidene)acetyl]oxime (**4b**, $C_{34}H_{26}NO_3P$)
Mp 148°C (acetone/*n*-hexane); yield 326 mg (62%); MS (EI): $m/e = 527$.

1,2-Diphenylethane-1,2-dione-O-[2-(triphenylphosphoranylidene)ethanethioyl]oxime (**4c**, $C_{34}H_{26}NO_2PS$)
Mp 145°C (acetone/*n*-hexane); yield 327 mg (60%); ^{1}H NMR (*DMSO*-d_6): $\delta = 5.6$ (d, 1H, $^2J_{PH} = 24$ Hz, CH=P), 7.45–7.65 (25H-aromat) ppm; ^{31}P NMR: $\delta = 25.90$ ppm; IR (KBr): $\bar{\nu} =$ 1700 (C=O), 1244 (C=S) cm^{-1}; MS (EI): $m/e = 544$.

1,2-Diphenylethane-1,2-dione-O-{triphenyl[2-(triphenyl-phosphoranylidene)methyl]phosphoranyl}oxime
(**6**, $C_{51}H_{41}NO_2P_2$)
To a solution of 225 mg **3** (1 mmol) in *THF* 20 cm^3, was added a solution of 536 mg **2** [12] (1 mmol) in 20 cm^3 *THF*. The reaction mixture was boiled for 6 h and the solvent was removed off. The residue was chromatographed on silica gel using *n*-hexane:*THF* (3:1, *v*/*v*) as an eluent. Upon heating of adduct **6** for 30 min in boiling toluene, it was recovered unchanged. mp 173°C (benzene); yield 532 mg (70%); MS (EI): $m/e = 224$ and 535.

(2-Oxa-1-aza-triphenylen-3-ylidene)phenylamine
(**9a**, $C_{22}H_{14}N_2O$)
To a stirred solution of 223 mg **7** [13] (1 mmol) in 20 cm^3 *THF*, was added dropwise within 30 min a solution of 377 mg **1a** [9] (1 mmol) in 20 cm^3 of the same solvent. The reaction mixture was further stirred for 8 h. After removing the solvent, the residue was chromatographed on silica gel using *n*-hexane:ethyl acetate (85:15, *v*/*v*) as an eluent, to give 225 mg (70%) **9a**, mp 147°C and 55 mg (20%) triphenylphosphine oxide; MS (EI): $m/e = 322$.

Phenanthrene-9,10-dione O-[2-(triphenylphosphoranyl-idene)acetyl]oxime (**8b**, $C_{34}H_{24}NO_3P$)
To a solution of 223 mg **7** (1 mmol) in 20 cm^3 of dry toluene, was added a solution of 302 mg **1b** (1 mmol) in 30 cm^3 toluene. The reaction mixture was refluxed for 8 h. After the solvent had been removed under reduced pressure, the residue was chromatographed on silica gel using *n*-hexane:acetone (3:1, *v*/*v*) as an eluent, to give 393 mg (75%) **8b**. Mp 246°C; ^{1}H NMR (*DMSO*-d_6): $\delta = 5.13$ (d, 1H, $^2J_{HP} = 24$ Hz, CH=P), 7.04–7.84 (23H-aromat) ppm; ^{31}P NMR: $\delta = 20.90$ ppm; IR (KBr): $\bar{\nu} = 1708$ (C=O, ester), 1644 (C=O, aryl) cm^{-1}; MS (EI): $m/e = 525$.

(2-Oxa-1-aza-triphenylen-3)-one (**9b**, $C_{16}H_9NO_2$)
When 525 mg of the phosphoranylidene adduct **8b** was heated in cold finger sublimator at 130°C for 30 min under reduced pressure (0.5 mm Hg), and the residue was chromatographed on silica gel using *n*-hexane:acetone (93:7, *v*/*v*) as an eluent, 70 mg (20%) triphenylphosphine oxide was isolated (mp and mixed mp 151°C), along with the oxazinone derivatives **9b**. Mp 122°C; yield 123 mg (50%); ^{1}H NMR (*DMSO*-d_6): $\delta = 4.01$ (s, 1H, oxazine), 7.27–7.75 (8H-aromat) ppm; ^{13}C NMR (*DMSO*-d_6): $\delta = 176.37$ (C=O), 163.05 (C=N) ppm; IR (KBr): $\bar{\nu} = 1699$ (C=O, Oxazine) cm^{-1}; MS (EI): $m/e = 247$.

Phenanthrene-9,10-dione O-[2-(triphenyl-phosphoranyl-idene)ethanethioyl]oxime (**8c**, $C_{34}H_{24}NO_2PS$)
A mixture of 319 mg **1c** (1 mmol), 223 mg of **7** (1 mmol) and 40 cm^3 toluene, was boiled for 12 h. The solvent was removed under reduced pressure and the residue that left was chromatographed on silica gel using *n*-hexane:acetone (55:45, *v*/*v*) as an eluent, to give 378 mg (70%) **8c**. Mp 176°C; ^{1}H NMR (*DMSO*-d_6): $\delta = 5.06$ (d, 1H, $^2J_{HP} = 27$ Hz, CH=P), 7.54–7.74 (23H-aromat) ppm; ^{31}P NMR: $\delta = 33.94$ ppm; IR (KBr): $\bar{\nu} = 1651$ (C=O), 1262 (C=S) cm^{-1}; MS (EI): $m/e = 541$.

Phenanthrene-9,10-dione-O-{triphenyl[(triphenyl-phosphoranylidene)methyl]phosphoranyl}oxime
(**10**, $C_{51}H_{39}NO_2P_2$)
A mixture of 536 mg **2** (1 mmol) and 223 mg of **7** in toluene was refluxed for 8 h. After removing the solvent, the residue was crystallized from benzene to give 303 mg (40%) **10**. Mp 166°C; ^{1}H NMR (*DMSO*-d_6): $\delta = 5.35$ (dd, 1H, $^2J_{1,2HP} = 27$, 33 Hz, CH=P), 7.41–7.64 (38H-aromat) ppm; ^{31}P NMR: $\delta = 25.82$ (P=C), 22.88 (O–P) ppm; IR (KBr): $\bar{\nu} = 1651$ (C=O) cm^{-1}; MS (EI): $m/e = 759$.

*Reaction of 1 methyl-1H-indole-2,3-dione 3-oxime (**11**) with the phosphacumulenes **1a–1c** and the phosphallene **2***
General procedure: To a solution of 176 mg **11** [14] (1 mmol) in 20 cm^3 *THF* was added a solution of **1a–1c** or **2** (1 mmol) in 30 cm^3 *THF*. The reaction mixture was stirred at room temperature for 6 h in case of **1a** and **1b** and refluxed for 8 h when **1c** and **2** were used. After the solvent had been removed under reduced pressure, the residue was chromatographed on silica gel using *n*-hexane/acetone, to give **12a**, **12b**, **12c**, and **13**.

1-Methyl-1H-indole-2,3-dione-3-{O-[N-phenyl-2-(triphenyl-phosphoranylidene)ethanimidoyl]oxime}
(**12a**, $C_{35}H_{28}N_3O_2P$)
Mp 212°C (acetone/*n*-hexane); yield 370 mg (67%); MS (EI): $m/e = 524$ (M^+–C=O) and 376 [$(Ph)_3$P=C=C=N-*Ph*].

1-Methyl-1H-indole-2,3-dione-3-{O-[2-(triphenyl-phosphoranylidene)acetyl]oxime} (**12b**, $C_{29}H_{23}N_2O_3P$)
Mp 230°C (acetone/*n*-hexane); yield 310 mg (65%); ^{1}H NMR (*DMSO*-d_6): $\delta = 3.33$ (s, 3H, CH_3), 5.6 (d, 1H, $^2J_{HP} = 27$ Hz, CH=P), 7.5 (19H-aromat) ppm; ^{31}P NMR: $\delta = 20.34$ ppm; IR (KBr): $\bar{\nu} = 1716$ (C=O, ester), 1649 (C=O, amide) cm^{-1}; MS (EI): $m/e =$ [278 (M^+-201) 201 (M^+-278 (TPPO))].

1-Methyl-1H-indole-2,3-dione-3-{O-[2-(triphenylphosphor-anylidene)ethanethioyl]oxime} (**12c**, $C_{29}H_{23}N_2O_2PS$)
Mp 178°C (acetone/*n*-hexane); yield 321 mg (65%); ^{1}H NMR (*DMSO*-d_6): $\delta = 3.35$ (s, 3H, CH_3), 5.05 (d, 1H, $^2J_{HP} = 27$ Hz, CH=P), 7.42 (19H-aromat) ppm; ^{31}P NMR: $\delta = 22.87$ ppm; IR (KBr): $\bar{\nu} = 1650$ (C=O), 1242 (C=S) cm^{-1}; MS (EI): $m/e = 494$.

1-Methyl-1H-indole-2,3-dione-3-{O-[triphenyl[(triphenyl-phosphoranylidene)methyl]phosphoranyl]oxime}
(**13**, $C_{46}H_{38}N_2O_2P_2$)
Mp 166°C (acetone/*n*-hexane); yield 469 mg (66%); ^{1}H NMR (*DMSO*-d_6): $\delta = 3.6$ (s, 3H, CH_3), 5.65 (dd, 1H, $^2J_{1,2HP} = 24$, 27 Hz, CH=P), 7.11–8.17 (34H-aromat) ppm; ^{31}P NMR: $\delta = 17.98$ (N–O–P), 22.91 (CH=P) ppm; IR (KBr): $\bar{\nu} = 1593$ (C=O, amide) cm^{-1}; MS (EI): $m/e = 713$.

(3-Phenylimino-3H-2-oxa-1-aza-fluoren-9)-one
(**16a**, $C_{17}H_{10}N_2O_2$)
A suspension of 175 mg indan-1,2,3-trione-2-oxime (**14**) [15] (1 mmol) and 377 mg **1a** (1 mmol) in *THF* (50 cm^3) was stir-

red at room temperature for 8 h. After evaporation of the solvent, the remainder was subjected to column chromatography on silica gel. Elution with *n*-hexane:ethyl acetate (9:1, *v*/*v*), afforded the oxazinone **16a**. Mp 137°C; yield 164 mg (60%); MS (EI): $m/e = 274$.

1H-Indene-1,2,3-trione-2-{O-[2-(triphenylphosphoranylidene)acetyl]oxime} (**15b**, $C_{29}H_{20}NO_4P$)
To a solution of 175 mg **14** (1 mmol) in 30 cm^3 *THF*, was added a solution of 302 mg **1b** (1 mmol) in 30 cm^3 of the same solvent, and the reaction mixture was stirred for 10 h at room temperature. After removing the solvent under reduced pressure, the residue was crystallized from benzene to give **15b**.

Mp 205°C; yield 295 mg (62%); ^{1}H NMR (*DMSO*-d_6): $\delta = 5.6$ (d, 1H, $^2J_{HP} = 24$ Hz, CH=P), 7.73 (19H-aromat) ppm; ^{13}C NMR (*DMSO*-d_6): $\delta = 197.28$ (C=O, ester), 195.28 (C=O, indanone), 165.41 (C=N), 146.37 (P=C) ppm; ^{31}P NMR: $\delta = 22.89$ ppm; IR (KBr): $\bar{\nu} = 1733$ (CO, ester), 1656 (C=O, indanone) cm^{-1}; MS (EI): $m/e = 278$[(M^+-199 oxazinone) 199 (M^+-278 TPPO)].

(2-Oxa-1-aza- fluorene)3,9-dione (**16b**, $C_{11}H_5NO_3$)
16b was obtained when the same reaction (compounds **14** and **1b**), was repeated in boiling toluene for 8 h, along with 70 mg (25%) triphenylphosphine oxide was obtained, too.

Mp 214°C (acetone/*n*-hexane); yield 135 mg (68%); ^{1}H NMR (*DMSO*-d_6): $\delta = 4.37$ (s, 1H, oxazinone), 7.55–7.91 (4H-aromat) ppm; ^{13}C NMR (*DMSO*-d_6): $\delta = 195.41$ (C=O, ester), 175.4 (C=O, indanone), 165.41 (C=N) ppm; IR (KBr): $\bar{\nu} = 1714$ (C=O, ester), 1653 (C=O, indanone) cm^{-1}; MS (EI): $m/e = 199$.

*Reaction of (2-thioxovinylidene)triphenylphosphorane (**1c**), or hexaphenylcarbodiphosphorane (**2**) with indan-1,2,3 trione-2-oxime (**14**)*
A mixture of 319 mg **1c** (1 mmol), or 536 mg **2** (1 mmol) with 175 mg the trione oxime **14** (1 mmol), in *THF* was refluxed for 6 h in case of **1c** and 8 h in case of **2**. After usual working up, the phosphoranylidenes, **15c** and **17** were isolated respectively.

1H-Indene-1,2,3-trione-2-{O-[2-(triphenylphosphoranylidene)ethanethioyl]oxime} (**15c**, $C_{29}H_{20}NO_3PS$)
Mp 260°C (ethyl acetate/*n*-hexane); yield 302 mg (62%); ^{1}H NMR (*DMSO*-d_6): $\delta = 5.13$ (d, 1H, $^2J_{HP} = 21$ Hz, CH=P), 7.51–7.70 (19H-aromat) ppm; ^{13}C NMR (*DMSO*-d_6): $\delta =$ 200.47 (C=S), 197.28 (C=O, indanone), 165.41 (C=N), 146.37 (P=C) ppm; ^{31}P NMR: $\delta = 22.91$ ppm; IR (KBr): $\bar{\nu} = 1716$ (C=O), 1164 (C=S) cm^{-1}; MS (EI): $m/e = 493$.

1H-Indene-1,2,3-trione-2-(O-{triphenyl[((triphenylphosphoranylidene)methyl]phosphoranyl}oxime
(**17**, $C_{46}H_{35}NO_3P_2$)
Mp 216°C (benzene); yield 568 mg (80%); ^{1}H NMR (*DMSO*-d_6): $\delta = 5.79$ (dd, H, $^2J_{1,2HP} = 22$, 33 Hz, CH=P), 7.51–7.70 (34H-aromat) ppm; ^{13}C NMR (*DMSO*-d_6): $\delta = 195.41$ (C=O, indanone), 163.05 (C=N) ppm; ^{31}P NMR: $\delta = 19.16$ (O–P), 22.91 (ylidic-P) ppm; IR (KBr): $\bar{\nu} = 1699$ (C=O) cm^{-1}; MS (EI): $m/e = 449$[M^+-262(Ph_3P)].

When the phosphoranylidenes **15c** or **17** were heated in a cold finger sublimator at 200°C for 30 min under reduced pressure (0.5 mm Hg), these adducts were recovered unchanged.

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