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Chemistry of phosphorus ylides. Part 25 [1]. Interaction of hexaphenylcarbodiphosphorane with carbonyls, hydrazone, and *Mannich* bases. A synthesis of phosphoranylidenes, phosphobetaines, and oxaphosphinin

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Abstract The reaction of the allylic hexaphenylcarbodiphosphorane with carbonyls afforded the corresponding phosphoranylidene derivatives. On the other hand, the stable phosphorbetaines were obtained when the bisphosphorane was allowed to react with the α-diketone and triketone. The azaphosphoranylidene was isolated from the reaction of the bisphosphorane with hydrazone. Moreover, the bisphosphorane reacted with niclosamide and quinoline *Mannich* bases with the formation of the oxaphosphinins. When the *Wittig* reaction was performed with the new phosphoranes, the corresponding exocyclic olefins were obtained. On the other hand, the oxaphosphinins were produced when the phosphoranes were treated under the condition of a *Hoffmann* degradation reaction.

Keywords Hexaphenylcarbodiphosphorane; Phosphoranylidenes; Phosphobetaines; Oxaphosphinins.

Introduction

The phosphallene ylide hexaphenylcarbodiphosphorane can be illustrated in two major resonance forms. The first resonance form **1A**, is similar to the familiar *Wittig* reagents and **1B** implies a molecule with heteroallene chemistry. In the scope of enhanced reactivity and versatility of its nucleophilic reactions, this bisylide can be considered as an important reagent used by *Bestmann* [2] in organic synthesis, in particular products which are often difficult to prepare by other methods. Moreover, it has attracted recent interest because of its importance as a C-donor ligand in organometallic chemistry and various transition metal complexes [3]. It gives coinage metal complexes with organometallic compounds [4] and has triboluminescent properties [5]. On the other hand, the ylide and its derivatives have different biological applications as fungicides for soil born-organisms and phytopathogenic fungi [6].

Moreover, they are used as antiparasitics, which control large number of helminthes in sheeps [7].

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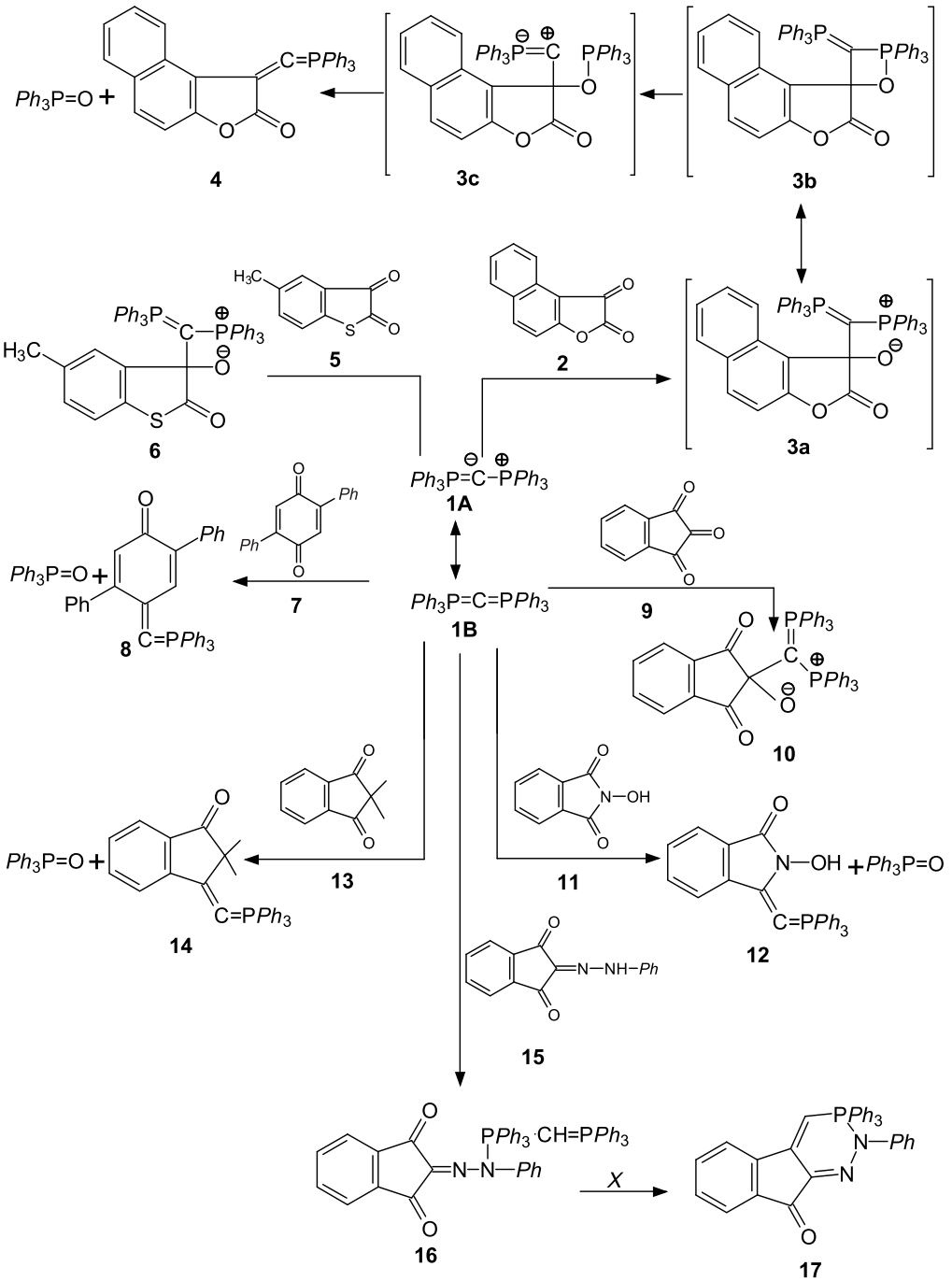
Results and discussion

As an ongoing program devoted to produce new bioactive heterocyclic phosphorus compounds [8], the reaction of hexaphenylcarbodiphosphorane (**1**), with α-diketones **2**, **5**, *p*-quinone **7**, triketone **9**, 2-hydroxyisoindole-1,3-dione (**11**), indandione **13**, hydrazone **15**, and *Mannich* bases **19** and **26** was studied.

Thus, naphtho[2,1-*b*]furan-1,2-dione (**2**), was treated with one mole equivalent of hexaphenylcarbodi-

phosphorane (**1**), in *THF* at room temperature for 3 h, and 3-[(triphenylphosphoranylidene)methylene]-naphtho[2,1-*b*]furan-2-one (**4**) together with triphenylphosphine oxide was isolated. The elemental microanalyses, IR, ^{13}C, ^{31}P NMR, and MS data agree with structure **4**. The IR spectrum showed strong absorption bands at $\bar{\nu} = 1610$ (C=O), 1560 (C=P) and 1440 cm^{-1} (P-phenyl) [9]. In the ^{13}C NMR spectrum of **4**, a signal was observed at $\delta = 165.00$ ppm, which is attributed to the lactone-carbonyl, no peak for the keto-carbonyl function, which appear in the starting material **2** at $\delta =$ 190.16 ppm [10]. A signal at $\delta = +20.50$ ppm was observed in the ^{31}P NMR which fits with phosphoranes [11], and in the mass spectrum, the M^+ was found at $m/z = 456$ (Scheme 1).



Scheme 1

It could be demonstrated that the formation of the phosphoranylidene **4** from the reaction of bis phosphorane **1** and benzocoumarandione **2** can be explained by initial nucleophilic attack of the carbanion center in the bisylide **1** on the reactive keto-carbonyl function in **2** rather than the lactone-carbonyl [12], to give the phosphobetaine **3a**, which is transformed to the four-membered unstable 1,2-oxaphosphetane intermediate **3b**. The original ylide C–P bond of **3b** is then cleaved to give the zwitterionic adduct **3c**. Triphenylphosphine oxide is eliminated with the formation of **4**.

When the bisphosphorane **1** was allowed to react with 5-methylbenzo[*b*]thiophene-2,3-dione (**5**), the reaction occurred at ambient temperature to give the stable phosphobetaine adduct **6**. The structure of the phosphobetaine **6**, was proved from analytical and spectroscopic data. Its IR spectrum showed bands at $\bar{\nu} = 1651$ (C=O, thio-lactone), 1608 (C=P), and 1481 cm^{-1} (P-phenyl). In the ^1H NMR spectrum of **6**, signals observed at $\delta = 2.25$ (s, 3H, CH_3) and $\delta = 7.5$ (m, 33H, aromatics) ppm. The ^{31}P NMR shifts recorded for compound **6** were $\delta = 20.49$ and 25.94 ppm. The values are in accord with ylidene phosphorane and betaine [11, 13]. In the MS of **6** the M^+ was found at $m/z = 714$.

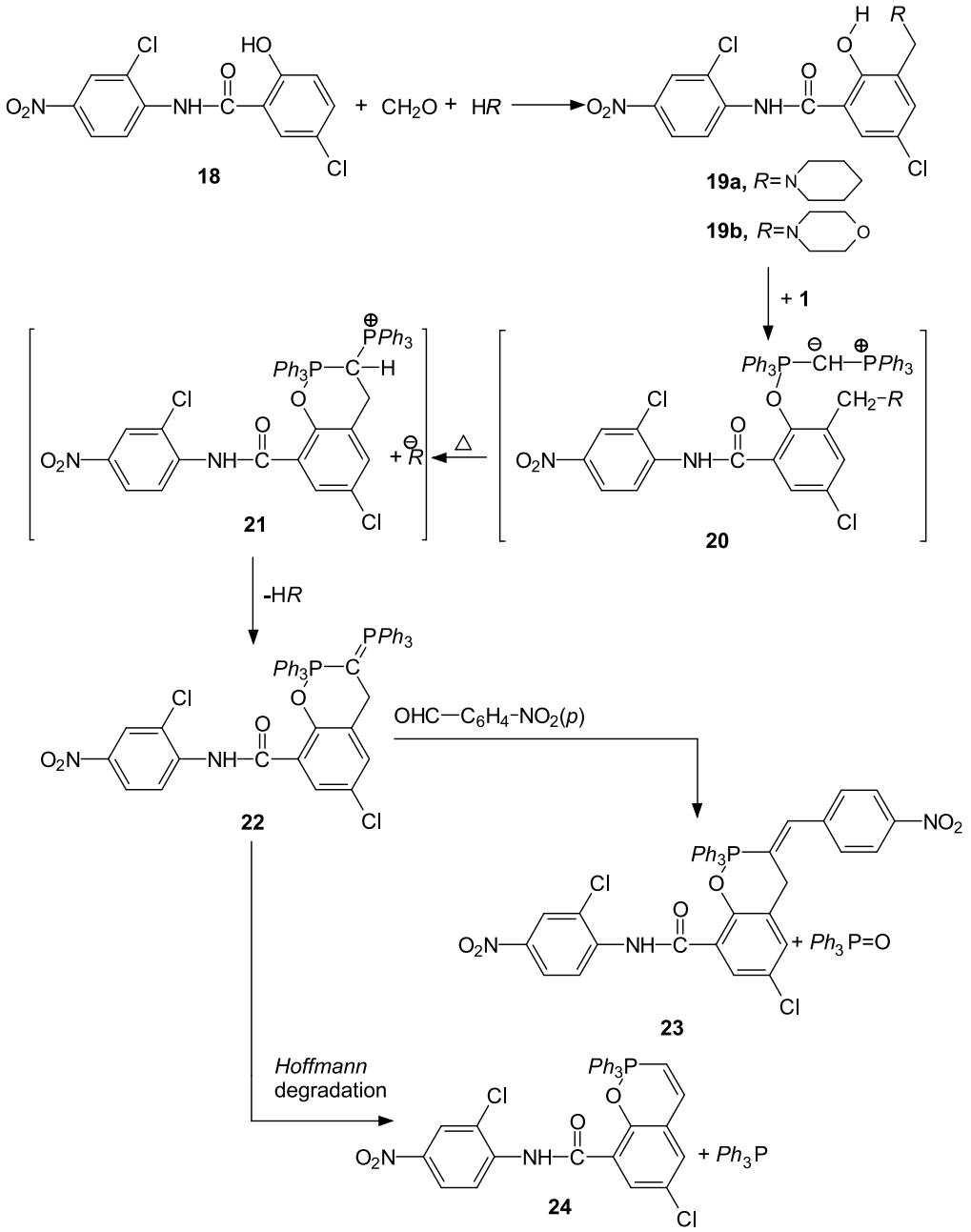
When 2,5-diphenyl-*p*-benzoquinone (**7**), was allowed to react with one mole or two moles of the bisphosphorane **1** under the same experimental conditions, only one product, namely, 2,5-diphenyl-4-[(triphenylphosphoranylidene)methylene]cyclohexa-2,5-diene-1-one (**8**) was isolated.

The reaction of vicinal triketone with **1** was investigated, too. When 1,2,3-indantrione (**9**), was allowed to react with the bisphosphorane **1**, the corresponding phosphobetaine adduct **10** was obtained.

In addition, we studied the behavior of the bifunctional compounds, 2-hydroxyisoindole-1,3-dione (**11**) and indane-1,3-dione (**13**), towards the bisphosphorane **1**. The reaction proceeded like in the case of the *p*-quinone **7**, with the formation of 2-hydroxy-3-(triphenylphosphoranylidene)methylene]-2,3-dihydroisoindol-1-one (**12**) and 3-[(triphenylphosphoranylidene)methylene]indan-1-one (**14**). No protonation reaction was observed with >N–OH and $>CH_2$ groups, even when two moles of the bisphosphorane **1** were used.

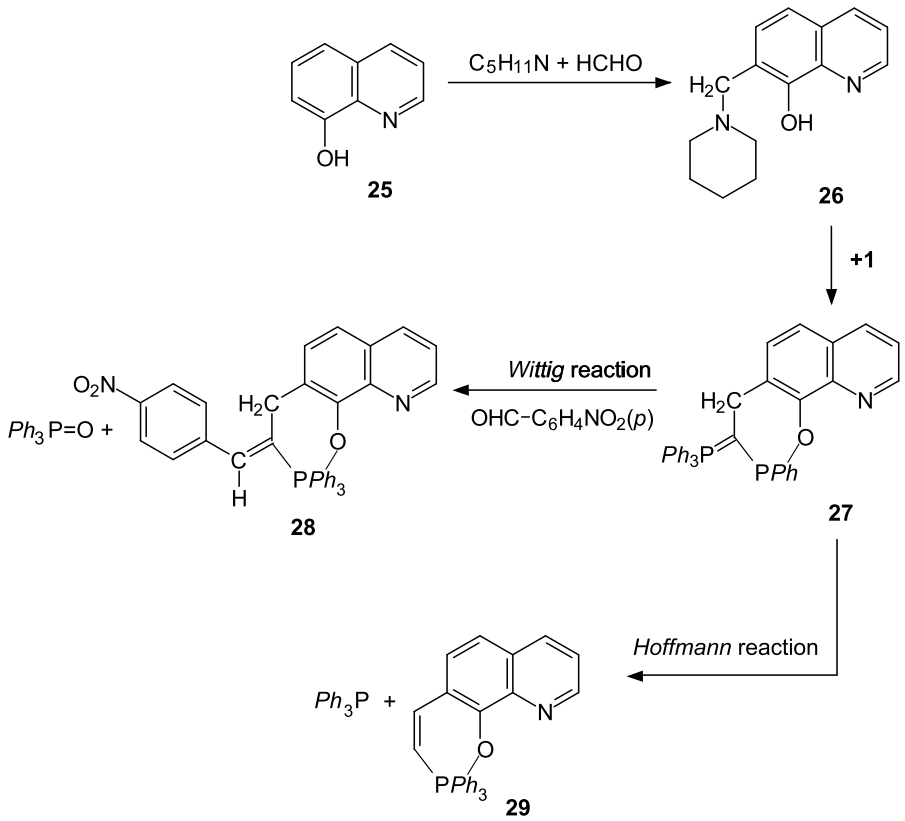
When 2-(phenylhydrazono)indan-1,3-dione (**15**) was treated with the bisphosphorane **1**, 2-[phenyl-[triphenyl[(triphenylphosphoranylidene)methyl]phosphino]hydrazono]indane-1,3-dione (**16**) was obtained as red crystals. The IR spectrum of **16** revealed the absence of NH group, and showed bands at $\bar{\nu} = 1690, 1650$ (C=O), 1590 (C=P), and 1490 cm^{-1} (P-phenyl). Moreover, the ^1H NMR of **16** showed signals at $\delta = 6.4$ (dd, 1H, $^2J_{HP} = 21$ Hz, CH=P) and $\delta = 7.4$ (m, 39H, aromatics) ppm. The ^{31}P NMR shifts recorded for **16** were $\delta = 17.44$ (P-ylidene) and $\delta = 26.06$ (P–N) ppm. The MS showed the molecular ion peak at $m/z = 786$.

Niclosamide, (5-chloro-*N*-(2-chloro-4-nitrophenyl)-2-hydroxybenzamide) (**18**), is the active ingredient of bayluscide, which has been used as molluscicide of great significance in the last decade [14]. It is widely used in control programmes, and is still the molluscicide of choice, since it is effective against most aquatic snails and its activity persists for several months. Also, it does not adversely affect any economically important crop plants and shows no cumulative toxicity on animals [15]. Niclosamide has been introduced as an official drug in many pharmacopoeas [16]. Therefore, the present investigation was extended to synthesize the niclosamide *Mannich* base derivatives **19a** and **19b**, and react them with the bisphosphorane **1** to prepare the new oxaphosphinin niclosamide derivative **22** of biological interest. The *Mannich* reaction was carried out in neutral media using the bifunctional niclosamide **18** as substrate, formaldehyde, piperidine, or morpholine as the reagents. When the bisphosphorane **1**, was allowed to react with niclosamide *Mannich* bases **19a** or **19b**, in dry boiling toluene for 4 h, the corresponding 6-chloro-*N*-(2-chloro-4-nitrophenyl)-3,4-dihydro-2,2,2-triphenyl-3-(triphenylphosphoranylidene)-2*H*-benzo[*e*]-1,2-oxaphosphin-8-carboxamide (**22**) was only obtained. The IR spectrum of **22** showed bands at $\bar{\nu} = 3397$ (NH), 1670 (CO, amide), 1570 (C=P), and 1436 (P-aryl) cm^{-1}. In the ^1H NMR spectrum of **22**, signals at $\delta = 3.45$ (d, $^3J_{PH} = 16$ Hz, CH_2), $\delta = 7.40$ (m, 35H, aromatics), and $\delta = 10.5$ (s, NH, exchangeable with D_2O) ppm were observed. The ^{31}P NMR shifts recorded for **22** were $\delta = 20.35$ (phosphoranylidene) and $\delta = 50.35$ (oxaphosphinin) ppm [2a]. Presence of the carbonyl amide group in **22** was also attested by a signal at $\delta = 163.05$ ppm in its ^{13}C NMR and the M^+ of **22** is at $m/z = 874$. Compound **22** is equally obtained irrespective whether one or two mole equivalents of the bisphosphorane **1** are used (Scheme 2).



Scheme 2

When the *Wittig* reaction [17] was carried out with the oxaphosphinin compound **22**, using 4-nitrobenzaldehyde, the new excocyclic olefin 6-chloro-*N*-(2-chloro-4-nitrophenyl)-3,4-dihydro-2,2,2-triphenyl-3-(4-nitrobenzylidene)-2*H*-benzo[*e*]-1,2-oxaphosphin-8-carboxamide (**23**), was isolated together with triphenylphosphine oxide. The IR spectrum of **23** showed bands at $\bar{\nu} = 3200$ (NH), 1650 (C=O), and 1430 cm^{-1} (P-aryl). The ^1H NMR spectrum of **23**, showed signals at $\delta = 3.84$ (s, CH_2), $\delta = 6.01$ (s, CH), $\delta = 7.51$ (m, 24H, aromatics) and $\delta = 10.5$ (s, NH, exchangeable with D_2O) ppm. A signal at $\delta = 50.34$ ppm was observed in the ^{31}P NMR of **23**, and m/z was found at 747 (M^+) in the mass spectrum. Under the condition of *Hoffmann* degradation reaction [18] in which **22** was heated for 45 min (110°C) under reduced pressure (0.5 mm Hg), the corresponding *N*-(2-chloro-4-nitrophenyl)(6-



Scheme 3

chloro-2,2,2-triphenylbenzo[*e*]-1,2-oxaphosphin-8-yl)carboxamide (**24**) was obtained. Compound **24** was formed *via* migration of the α-proton in **22**, with expulsion of triphenylphosphine. The IR spectrum of **24**, revealed the presence of strong absorption bands at $\bar{\nu} = 3293$ (NH), 1663 (C=O, amide), and 1494 cm^{-1} (P-phenyl). In the ^1H NMR spectrum of **24**, signals appeared at $\delta = 7.61$ (m, 22H, aromatics) and $\delta = 10.5$ (s, NH, exchangeable with D_2O) ppm. Moreover, one signal at $\delta = 50.39$ ppm was observed in its ^{31}P NMR spectrum, and the mass spectrum showed a peak at $m/z = 613$ $(M + H)^+$.

8-Hydroxyquinoline (**25**) has been found effective in controlling photodegradation of the Neem based pesticide azadirachtin-A derivatives [19]. Moreover, its derivatives are used as antimalarial drugs [20], and their copper complexes are useful as chemotherapeutic agents [21]. Furthermore, they have also been tested for their antiretroviral activity in HIV-1 infected cells [22]. Therefore, it was of interest to study the reaction of the bisphosphorane **1** with the 8-hydroxyquinoline *Mannich* base **26** to prepare oxaphosphinoquinoline derivatives of anticipated biological and industrial interest. When 7[piperidin-1-yl)methyl]quinolin-8-ol (**26**) was treated with one mole equivalent of the bisphosphorane **1**, the corresponding triphenyl(3,4-dihydro-2,2,2-triphenyl-2*H*-1,2-oxaphosphino[5,6-*h*]quinolin-3-ylidene)-phosphine (**27**) was obtained. 3,4-Dihydro-2,2,2-triphenyl-3-(4-nitrobenzylidene)-2*H*-1,2-oxaphosphino[5,6-*h*]quinoline (**28**) was obtained when **27** was treated with 4-nitrobenzaldehyde under the condition of a *Wittig* reaction. When **27** was heated for 45 min (160°C) under reduced pressure (0.5 mm Hg), the new 2,2,2-triphenyl-2*H*-1,2-oxaphosphino[5,6-*h*]-quinoline (**29**) was isolated.

Conclusions

The results of the present investigation represent an interesting approach to the synthesis of new bioactive heterocyclic phosphorus compounds by direct routes. It can be rationalized that the reaction of hexaphenylcarbodiphosphorane (**1**), with the α-diketones **2** and **5**, *p*-quinone **7**, and triketone **9** occurs by a [2 + 2] cycloaddition of the reactive carbonyl

group to the ylidic C=P of the bisphosphorane **1** to yield the phosphobetaines, which are stable like compounds **6** and **10**.

On the other hand, the intermediate betains of the starting materials **2** and **7** are unstable and transformed to the phosphoranylidenes **4** and **8** with the elimination of triphenylphosphine oxide. In the case of the bifunctional compounds **11** and **13**, the reaction proceeded like in the case with *p*-quinone **7** with the formation of the phosphoranylidenes **12** and **14**, even when two moles of the bisphosphorane **1** are used. In the case of the 1:1 adduct **16** produced from the reaction of the (phenylhydrazono)indandione (**15**) and the bisphosphorane **1**, this adduct was recovered practically unchanged under the condition of intramolecular *Wittig* olefination and no diazaphosphinin **17** and triphenylphosphine oxide were obtained. On the other hand, the bisphosphorane **1** reacted readily with the phenolic OH group of the *Mannich* base **19** to give firstly the phosphorus ylide **20**, which is transformed into the intermediate **21** by nucleophilic substitution of the dialkylamine anion. Elimination of the amine from **21** afforded the oxaphosphinin **22**. In addition, the new heterocyclic phosphorus compounds, oxaphosphinins **23**, **24**, **28**, and **29** were obtained by applying the *Wittig* and *Hoffmann* degradation reactions on **22** and **27**. These processes can be considered as new and simple routes for the preparation of different ring systems, which can not be obtained by other conventional methods.

Experimental

All melting points were measured on a Gallenkamp electrothermal melting point apparatus. The infrared spectra were recorded using KBr pellets on a 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 external reference. Mass spectra were recorded on a Shimadzu GC-MS QP 1000 Ex Spectrometer (EI, 70 eV). Elemental analyses were carried out at Microanalytical center of National Research Center, El-Tahrir Street, Dokki, Cairo. The results were in agreement with the calculated values.

*Reaction of hexaphenylcarbodiphosphorane (**1**) with carbonyls **2**, **5**, **7**, **9**, **11**, **13**, and hydrazone **15**. Synthesis of phosphoranylidenes **4**, **8**, **12**, **14**, phosphobetaines **6**, **10**, and azaphosphoranylidene **16***

A solution of hexaphenylcarbodiphosphorane (**1**) [23] (0.01 mol) in 50 cm^3 *THF* was added with stirring at room temperature to the solution of carbonyls **2**, **5**, **7**, **9**, **11**, **13**, or hydrazone **15** (0.01 mol) in 50 cm^3 *THF*. The reaction mixture was stirred from 3 to 6 h until no more of the starting materials could be detected (TLC). *THF* was distilled off under reduced pressure and the remaining residue was crystallized from the appropriate solvent to give the phosphoranylidenes **4**, **8**, **12**, **14**, phosphobetaines **6**, **10**, or azaphosphoranylidene **16**. When the reaction was repeated using one mole of carbonyls **2**, **5**, **7**, **9**, **11**, **13**, or hydrazone **15** and two moles of the hexaphenylcarbodiphosphorane (**1**) the same products were isolated of phosphoranylidenes **4**, **8**, **12**, **14**, betaines **6, 10**, or azaphosphoranylidene **16**.

3-[(Triphenylphosphoranylidene)methylene]naphtho[2,1-b]-furan-2-one (**4**, $C_{31}H_{21}O_2P$)
Mp 182°C (benzene/pet.ether.); yield 85% (yellow crystals).

2,5-Diphenyl-4-[(triphenylphosphoranylidene)methylene]-cyclohexa-2,5-diene-1-one (**8**, $C_{37}H_{27}OP$)
The residue was chromatographed on silica gel using pet.-ether/acetone as eluent (50/50, *v*/*v*) and yielded the phosphoranylidene **8**. It was recrystallized from cyclohexane. Mp 198°C; yield 60% (buff crystals); IR: $\bar{\nu} = 1791$ (C=O), 1630 (C=P), 1471 (P-phenyl) cm^{-1}; ^{13}C NMR: $\delta = 178.74$ (C=O) ppm; ^{31}P NMR: $\delta = 20.03$ ppm; MS: $m/z = 518$ (M^+).

2-Hydroxy-3-[(triphenylphosphoranylidene)methylene]-2,3-dihydroisoindol-1-one (**12**, $C_{27}H_{20}NO_2P$)
Purification on silica gel column using pet-ether/acetone (65/35, *v*/*v*) as an eluent yielded phosphoranylidene **12**. It was recrystallized from *n*-hexane. Mp 128°C; yield 60% (orange crystals); IR: $\bar{\nu} = 3434$ (OH), 1699 (C=O), 1681 (C=P), 1488 (P-phenyl) cm^{-1}; ^{1}H NMR: $\delta = 7.5$ (m, 19H, aromatics), 9.8 (s, 1H, OH, exchangeable with D_2O) ppm; ^{31}P NMR: $\delta = 20.47$ ppm; MS: $m/z = 420$ $(M–H)^+$.

3-[(Triphenylphosphoranylidene)methylene]indan-1-one (**14**, $C_{28}H_{21}OP$)
Mp 175°C (benzene); yield 40% (violet crystal); IR: $\bar{\nu} = 1610$ (C=O) cm^{-1}; ^{1}H NMR: $\delta = 3.70$, 7.5 (m, 19H, aromatic) ppm; ^{31}P NMR $\delta = 20.51$ ppm; MS: $m/z = 403$ $(M–H)^+$.

2,3-Dihydro-5-methyl-2-oxo-3-[(triphenylphosphinio)-(triphenylphosphoranyliden)methyl]benzo[b]thiophene-3-olat (**6**, $C_{46}H_{36}O_2P_2S$)
Mp 150°C (chloroform/pet.ether.); yield 70% (pink crystals).

1,3-Dioxo-2-[(triphenylphosphinio)(triphenylphosphoranyliden)methyl]indan-2-olat (**10**, $C_{16}H_{34}O_3P_2$)
Mp 142°C (benzene/pet.ether.); yield 40% (brown crystals); IR: $\bar{\nu} = 1777$, 1718 (C=O), 1588 (C=P), 1479 (P-phenyl) cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 7.8$ (m, 19H, aromatics) ppm; ^{31}P NMR: $\delta = 20.51$ (P-ylidene), 26.00 (P-betaine) ppm; MS: $m/z = 695$ $(M–H)^+$.

2-[Phenyl-[1,1,1-triphenyl]phosphino]hydrazono-[(triphenylphosphoranylidene)-methyl]indane-1,3-dione (**16**, $C_{52}H_{40}N_2O_2P_2$)
Mp 223°C, yield 75% (red crystals).

*Attempted cyclization of azaphosphoranylidene (**16**)*
When **16** was boiled in toluene for 12 h or heated alone at 180°C for 1 h under reduced pressure (0.5 mm Hg), neither diazaphosphinin **17** nor triphenylphosphine oxide were obtained, and **16** was recovered practically unchanged.

*Mannich reaction on niclosamide [5-chloro-N-(2-chloro-4-nitrophenyl)]-2-hydroxybenzamide (**18**)*
An aqueous solution of formaldehyde (40%, 0.01 mol) was added dropwise with stirring to a solution of niclosamide (**18**) [24] and the amine (piperidine or morpholine) (0.011 mol) in about 40 cm^3 of ethanol, while maintaining the temperature below 10°C. The reaction mixture was then boiled under reflux for 2 h, and left overnight at room temperature. After removing the volatile materials under reduced pressure, the product was isolated and recrystallized from ethanol. When the above described procedure was performed using two mole equivalents of both of the base and aqueous formaldehyde no change in the nature of the products was observed and the corresponding niclosamide *Mannich* bases **19a** and **19b** were obtained.

5-Chloro-N-(2-chloro-4-nitrophenyl)-2-hydroxy-3-(piperidinomethyl)benzamide (**19a**, $C_{19}H_{19}Cl_2N_3O_4$)
Mp 232°C (acetone/*n*-hexane); yield 87% (yellow powder); IR (KBr): $\bar{\nu} = 3422$ (OH), 3222 (NH), 2633(CH_2), 1655 (C=O, amide) cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 2.5$ (t, 4H, 2 CH_2 morpholin), 3.0 (t, 4H, 2 CH_2 morpholin), 3.5 (s, 2H, CH_2), 4.4 (s, H, NH), 8.6 (OH), 7.8 (m, 5H, aromatics) ppm; MS: $m/z = 424$.

5-Chloro-N-(2-chloro-4-nitrophenyl)-2-hydroxy-3-(morpholinomethyl)benzamide (**19b**, $C_{18}H_{17}Cl_2N_3O_5$)
Mp >300°C (ethanol); yield 95% (yellow powder); IR (KBr): 3422 (OH), 3222 (NH), 2633(CH_2), 1671 (C=O, amide) cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 2.5$ (t, 4H, 2CH_2 morpholin), 3.0 (t, 4H, 2CH_2 morpholin), 3.5 (s, 2H, CH_2), 4.4 (s, H, NH), 8.6 (OH), 7.8 (m, 5H, aromatics) ppm; MS: $m/z = 426$.

*The reaction of niclosamide Mannich base **19a** with hexaphenylcarbodiphosphorane (**1**). 6-Chloro-N-(2-chloro-4-nitrophenyl)-3,4-dihydro-2,2,2-triphenyl-3-(triphenylphosphoranylidene)-2H-benzo[e]-1,2-oxaphosphin-8-carboxamide* (**22**, $C_{51}H_{38}Cl_2N_2O_4P_2$)
A mixture of niclosamide *Mannich* base **19a** (0.01 mol), 5.3 g hexaphenylcarbodiphosphorane (**1**) (0.01 mol), and 40 cm^3 toluene was boiled for 6 h until no more of the starting materials could be detected. Toluene was removed under vacuum and the residue that remained was crystallized from ether/pet.ether to give oxaphosphinin **22**. Mp >300°C (ether/pet.ether); yield 70% (brown crystals). When the reaction was repeated using one mole of the second niclosamide *Mannich* base **19b** and hexaphenylcarbodiphosphorane (**1**), the same oxaphosphinin **22** was obtained.

6-Chloro-N-(2-chloro-4-nitrophenyl)-3,4-dihydro-2,2,2-triphenyl-3-(4-nitrobenzylidene)-2H-benzo[e]-1,2-oxaphosphin-8-carboxamide (**23**, $C_{40}H_{28}Cl_2N_3O_6P$)
A mixture of oxaphosphinin **22** (0.01 mol) and 4-nitrobenzaldehyde (0.01 mol) in dry toluene was refluxed for 10 h. Toluene was distilled off and the residue was crystallized from benzene/pet.ether to give the exocyclic olefin. Mp 197°C (benzene/pet.ether); yield 65% (orange crystals). The benzene filtrate afforded upon concentration and addition of pet.ether, colorless crystals of triphenylphosphine oxide (mp and mixed mp 151°C) [25].

N-(2-Chloro-4-nitrophenyl)-6-chloro-2,2,2-triphenyl-2H-benzo[e]-1,2-oxaphosphin-8-carboxamide
(**24**, $C_{33}H_{23}Cl_2N_2O_4P$)
When 0.6 g oxaphosphinin **22** were heated in an oil bath for 45 min at 110°C under reduced pressure (1 mm Hg) the residue was triturated with ether, filtered off, and recrystallized from chloroform/pet.ether to give 0.3 g of the oxaphosphinin derivative **24**. Mp 202°C (chloroform/pet.ether); yield 50% (buff crystals). Triphenylphosphine was isolated from the filtrate upon concentration. (mp and mixed mp 78°C).

Triphenyl(3,4-dihydro-2,2,2-triphenyl-2H-1,2-oxaphosphino-[5,6-h]quinolin-3-ylidene)phosphine (**27**, $C_{47}H_{37}NOP_2$)
To a solution of 5.36 g hexaphenylcarbodiphosphorane (**1**) (0.01 mol) in 20 cm^3 dry toluene, was added a solution of 2.42 g 8-hydroxyquinoline *Mannich* base (**26**) [26] (0.01 mol) in 30 cm^3 of dry toluene. The reaction mixture was refluxed for 6 h. After the solvent was distilled off under reduced pressure, the residue was recrystallized from ether/pet.ether to provide 3.46 g of oxaphosphinoquinoline (**27**). Mp 142°C; yield 65% (brown crystal); ^1H NMR: $\delta = 3.36$ (d, $^3J_{HP} = 16.5$ Hz, CH_2), 7.69 (m, 35 H, aromatics) ppm; ^{31}P NMR: $\delta = 20.33$ (phosphoranylidene) $\delta = 50.34$ (oxaphosphinin) ppm; MS: $m/z = 692$ $(M-H)^+$.

3,4-Dihydro-2,2,2-triphenyl-3-(4-nitrobenzylidene)-2H-1,2-oxaphosphino[5,6-h]quinoline (**28**, $C_{36}H_{27}N_2O_3P$)
A mixture of 0.64 g oxaphosphinoquinoline **27** (0.01 mol) and 1.7 g 4-nitrobenzaldehyde in 50 cm^3 toluene was refluxed for 10 h. Toluene was distilled off and the residue was crystallized from benzene to give 0.56 g of the exocylic olefin. Mp 202°C (benzene/pet.ether); yield 65% (yellow crystal). The distinguishing features of the ^1H NMR spectrum of **28**, were the presence of signals at $\delta = 3.38$ (s, CH_2), 6.51 (s, =CH), 7.65 (m, 24H, aromatics) ppm; ^{31}P NMR: $\delta = 50.34$ ppm; MS: $m/z = 565$ $(M-H)^+$. The benzene filtrate afforded upon concentration and addition of *n*-hexane, colorless crystals of triphenylphosphine oxide, mp 151°C [25].

2,2,2-Triphenyl-2H-1,2-oxaphosphino[5,6-h]quinoline
(**29**, $C_{29}H_{22}NOP$)
Oxaphosphinoquinoline **27** (0.69 g, 1 mmol) was heated for 45 min at 160°C under reduced pressure (0.5 mm Hg) until

no more of the starting material could be detected (TLC). The residue that remained was recrystallized from CH_2Cl_2/pet.ether to give 0.43 g **29**. Mp 216°C (CH_2Cl_2/pet.ether); yield 30% (buff powder); ^{31}P NMR: $\delta = 55.40$ ppm; MS: $m/z = 431$ (M^+). The dichloromethane filtrate afforded colorless crystals of triphenylphosphine upon concentration and addition of pet.ether mp 78°C.

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