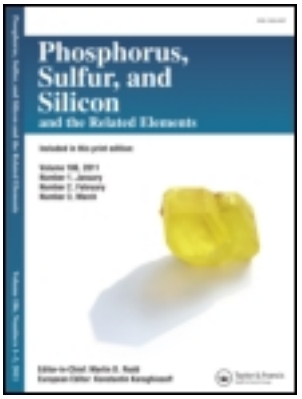

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Chemistry of Phosphorus Ylides. Part 36 Reactions of 2-Hydroxyisoindole-, Isoindoline-, and Indane-1,3-Dione With Stable and Active Phosphonium Ylides

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CHEMISTRY OF PHOSPHORUS YLIDES. PART 36 REACTIONS OF 2-HYDROXYISOINDOLE-, ISOINDOLINE-, AND INDANE-1,3-DIONE WITH STABLE AND ACTIVE PHOSPHONIUM YLIDES

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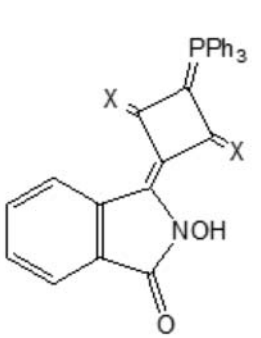
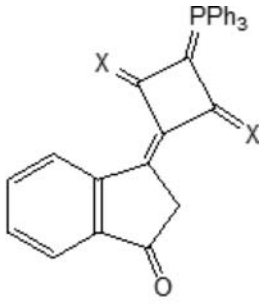
GRAPHICAL ABSTRACT



7a, X = N -C_6H_5
b, X = O



11a, X = N-C_6H_5
b, X = O

Abstract *The stabilized alkylidenephosphoranes namely, acetyl-, benzoyl-, methoxycarbonyl-, and ethoxycarbonyl-methylenetriphenylphosphorane react with 2-hydroxyisoindole-1,3-(2H)dione to give the corresponding isoindoline-ylidenes, along with triphenylphosphane oxide. On the other hand, the reaction of active phosphacumulenes, (N-phenyliminovinylidene)-, and (2-oxovinylidene)-triphenylphosphorane with hydroxyisoindole-, isoindoline-, and indane-1,3-dione afforded phosphanylidenecyclobutylidenes derivatives, together with triphenylphosphane oxide. Mechanisms accounting for the formation of the new products are discussed. The antimicrobial activities for the new compounds are also reported.*

Supplemental materials are available for this article. Go to the publisher's online edition of Phosphorus, Sulfur, and Silicon and the Related Elements *to view the free supplemental file.*

Keywords Isoindolinones; stable phosphonium ylides; phosphacumulenes; phosphanylidenecyclobutylidene derivatives; antimicrobial activities

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INTRODUCTION

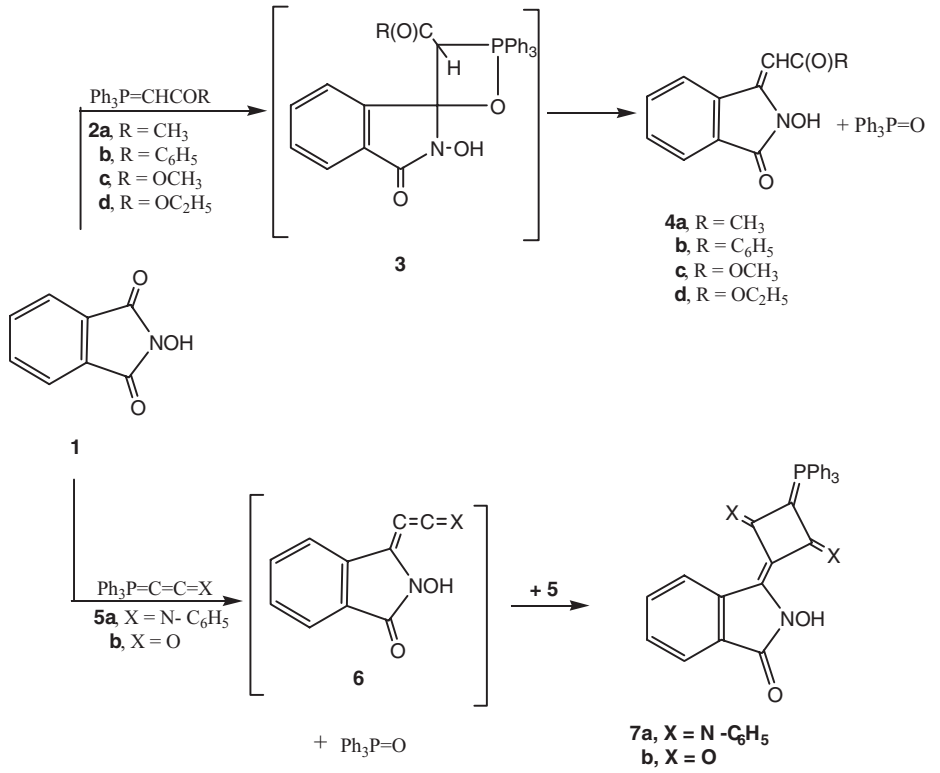
1,3-Indanedione derivatives have attracted considerable interest due to their anticoagulant, parasiticidal, herbicidal,[1] analgesic, and antimicrobial activities.[2] Moreover, they have found broad applications as adrenergic receptor antagonists.[3] On the other hand, N-substituted indane-1,3-diones have proven to be potent cytotoxic agents effective against the growth of single cell leukemia tumors and cell lines derived from solid tumors.[4,5] Our interest in the reactions of phosphonium ylides,[6,7] led us to investigate the behavior of these stabilized carbanions toward 2-hydroxyisoindole-1,3(2*H*)dione (**1**). The reaction of the active phosphacumulenes **5a**,**b** with the hydroxyisoindole-(**1**), isoindoline-(**8**), and indane-1,3-dione (**10**) was investigated, to prepare new phosphanylidenecyclobutylidene derivatives of anticipated antitumor activity.

RESULTS AND DISCUSSION

When 2-hydroxyisoindole-1,3(2*H*)dione (**1**) was treated with equimolar amounts of acetyl-(**2a**), benzoyl-(**2b**), methoxycarbonyl-(**2c**), or ethoxycarbonylmethylenetriphenylphosphorane (**2d**) in refluxing dry toluene for 3 h, the corresponding isoindoline ylidenes **4a–d** together with triphenylphosphane oxide were isolated. A [2+2]-cycloaddition of the C=O bond of compound **1** to the ylidic C–P bond of **2a–d** is proposed to generate the unstable oxaphosphetane **3**.[8–10] In the case of weakly nucleophilic stabilized ylides **2a–d**, the first stage of the reaction is the threobetaine, which is more stable than the erythrobetaine.[11,12] By this means, subsequent formation of the intermediate four-membered ring[13] and its decomposition into the trans olefin[14] and triphenylphosphane oxide are mainly formed.

The structure of the new compounds **4a–d** is assignable from their analyses, IR, ^{1}H, ^{13}C NMR and mass spectral (MS) data. The IR spectrum of **4a**, (KBr, ν, cm^{-1}) taken as an example, showed the OH group at 3245, the CO–CH_3 at 1791, and isoindolone CO at 1668. The most important feature of structure **4a** is the presence of signals at δ 2.62 (s) for the methyl protons, 5.95 (s) for the methine proton, 7.45–7.65 (m) for the aromatic protons, and the OH group gave rise to a signal at 7.91 ppm, which disappeared upon addition of D_2O in its ^{1}H NMR spectrum. The ^{13}C NMR spectrum of **4a** ($CDCl_3$) displayed distinct resonances of the methyl group at δ 30.0, the CH methine at 109.6, the isoindolone CO at 157.5, and the acetyl CO at 197.5 ppm. The MS indicated the presence of an ion peak at *m*/*z* (%): 204 [(M^++H), 100]. The structure of **4a** is also assigned on the basis of elemental analysis (Scheme 1).

The phosphacumulene ylides **5a**,**b**, are potentially useful building blocks used for the synthesis of phosphorus substituted carbocycles.[15] As part of our interest in these active phosphorus reagents,[15–22] we described here the behavior of (*N*-phenyliminovinylidene)-(**5a**), (2-oxovinylidene)-triphenylphosphorane (**5b**), toward the bifunctional compound 2-hydroxyisoindole-1,3-(2*H*)dione (**1**). When 1 mol equivalent of compound **1** was treated with 2 mol equivalents of the phosphorus reagent **5a** in tetrahydrofuran (THF) at room temperature for 3 h, phosphanylidenecyclobutylidenisoindoline **7a**, along with triphenylphosphane oxide was obtained. Formation of the phosphanylidene **7a** is proposed to occur by initial nucleophilic attack of the carbanion center in the ylide **5a** on the carbonyl function rather than the OH group in **1**, to give the unstable oxaphosphetane,[19,21–24] which decomposed to triphenylphosphane oxide and the unstable ketene **6**.[24] A second molecule of the ylide **5a** was added to the ketene **6**, to give the stable phosphanylidenecyclobutylidene **7a**.



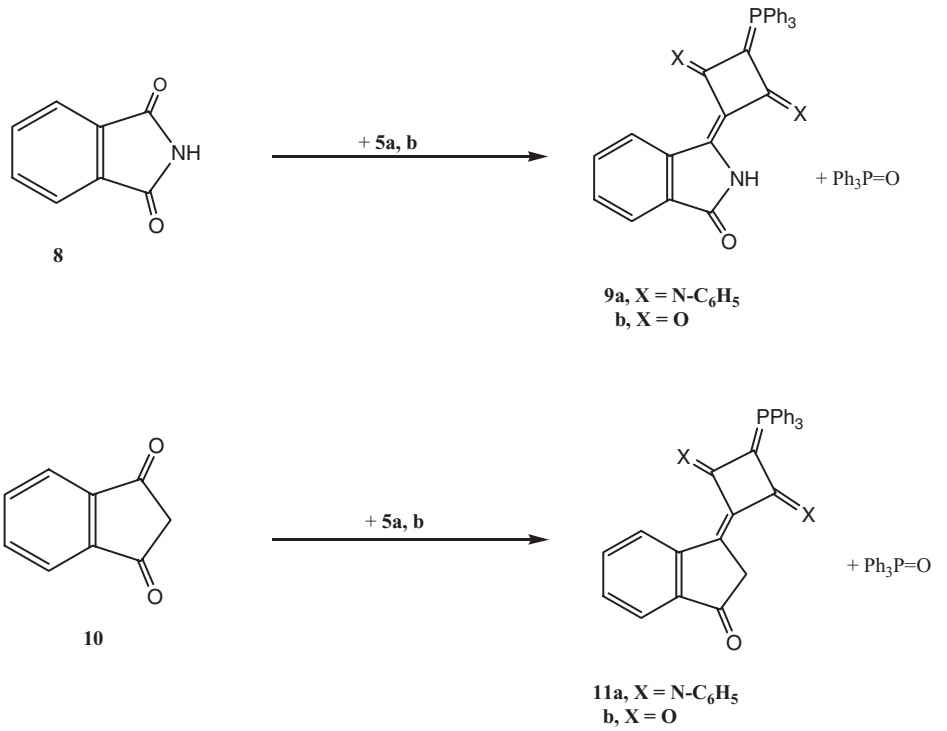
Scheme 1

The assignment of the proposed structure **7a** was based on the following observations. The IR spectrum of **7a** (KBr, ν cm^{-1}) showed the OH stretching vibration at 3400, the CO at 1670, the C═N at 1630, C═P at 1610,[25] and 1443 (P-phenyl).[26] The ^{1}H NMR spectrum of **7a** ($CDCl_3$) showed the OH signal at δ 10.22, which disappeared upon addition of D_2O, and at 7.45–7.65 ppm (m, 29H, arom-H). The ^{13}C NMR spectrum of **7a** ($CDCl_3$) showed the presence of signals at δ 160.3 (C═O), 167.6 (C═N), and 145.6 ppm (d, $^1J_{CP} = 95.7$ Hz, C═P). Moreover, a signal at δ 19.7 ppm was observed in its ^{31}P NMR spectrum, which fits for a phosphanyl group at a four-membered ring (Scheme 1).[27,28]

The reaction of compound **1** with the phosphorane reagent **5b** was performed in dry boiling toluene. The phosphanylidenecyclobutylidene derivative **7b** together with triphenylphosphane oxide was produced. Compound **7b** was identified on the basis of its IR, ^{1}H, ^{13}C, ^{31}P NMR, and MS data. The ^{1}H NMR and ^{31}P NMR of **7b** are shown in Figures S1 and S2 (available online in Supplemental Materials).

The reaction of isoindoline-1,3-dione (**8**), with the active phosphacumulenes **5a**,**b** was also studied. The reaction proceeded in THF at room temperature for 4 h in case of **5a**, and in boiling toluene for 6 h in case of **5b** to give the corresponding phosphanylidenecyclobutylidenisoindole derivatives **9a** and **9b**, respectively. Triphenylphosphane oxide was also isolated and identified (mp and mixed mp) (Scheme 2).

Finally, the reaction of indane-1,3-dione (**10**) with the active ylides **5a** and **5b** was performed to give triphenylphosphane oxide and the indene phosphanylidenecyclobutylidene derivatives **11a** and **11b**, respectively (Scheme 2).



Scheme 2

Structural assignment for compounds **9a**, **9b**, **11a**, and **11b** was based upon elemental analyses and spectroscopic data (IR, ^{1}H, ^{13}C, ^{31}P NMR, and MS).

CONCLUSION

The reaction of the bifunctional 2-hydroxyisoindole-dione **1** with the stabilized phosphonium ylides **2a**–**d** differs markedly from that of the respective active phosphacumulenes **5a**,**b**. Although, the initial step in these reactions is nucleophilic attack by the carbanion center of the phosphorane at the carbonyl group rather than the hydroxyl group, the consequences of reaction varied markedly according to the structure of these phosphoranes. While the stabilized phosphonium ylides afforded the isoindoline-ylidenes **4a**–**d**, the active phosphacumulenes gave the phosphanylidenecyclobutylideneisoindoles **7a** and **7b**. Moreover, the difference in the nucleophilic character of (*N*-phenyliminovinylidene)-(**5a**), and (2-oxovinylidene)-triphenylphosphorane (**5b**) can be observed too, (**5a** > **5b**).[29] While **5a** reacts smoothly with **1**, **8**, and **10**, the oxo analogue reacts less rapidly.

BIOLOGICAL EVALUATION OF THE TESTED COMPOUNDS

Biological Screening

The antibacterial and antifungal activities were carried out in the Microbial Department, National Research Centre, using the diffusion plate method.[30–33]

Antibacterial and Antifungal Activities

The antimicrobial activity of the tested compounds was examined against Gram-positive bacteria *Bacillus subtilis*, *Bacillus cereus*, and *Staphylococcus aureus*, Gram-negative bacteria *Escherichia coli*, *Pseudomonas aeruginose*, and *Salmonella*, and fungus *Candida albicans.* The obtained results are compared with the reference antibiotics[30–33] that were purchased from Egyptian markets.

Conclusion

From Tables S1 and S2 (available online in Supplemental Materials), compound **4b** was the only compound that exhibited antibiological activity against all the tested microorganisms (both Gram-positive and Gram-negative bacteria in addition to *Candida albicans* fungus) with nearly 50% efficiency compared to the reference antibiotic with the same concentration (mg/mL). It is worth noting that the starting material **1** and **2b** have no antimicrobial activity, but the product **4b** showed remarkably positive antimicrobial activities. Excellent inhibition (clear zone) to *Salmonella* pathogen was achieved by both **11b** and **4d** compounds knowing that their starting compounds (**10**, **5b**) and (**1**, **2d**) have no antibiological activity against this pathogen. The clear inhibition zone reached 20 mm in case of **11b**, that is, equivalent to the strength of the reference antibiotic, while it exceeds twice the activity of it in case of compound **4d**. Other tested compounds resulted in moderate different antibiological activities.

EXPERIMENTAL

Melting points (mp) were measured in open glass capillaries using Electrothermal IA 9100 series digital melting point apparatus (Electrothermal, Essex, UK). The IR spectra were recorded in KBr pellets on a Pye Unicam SP 3300 and Shimadzu FT IR 8101 PC infrared spectrophotometers (Pye Unicam Ltd. Cambridge, England and Shimadzu, Tokyo, Japan, respectively). The ^{1}H, ^{13}C NMR spectra were obtained from a JEOL ECA 500 MHz NMR spectrometer (Tokyo, Japan) using $CDCl_3$ as a solvent and tetramethylsilane (TMS) as an internal reference at 500.14, 125.76 MHz, respectively, and the ^{31}P NMR spectra were obtained from a JEOL ECA 500 MHz spectrometer at 200.4 MHz NMR spectrometer using H_3PO_4 (85%) as an external reference. Mass spectra (EI-MS) were recorded at 70 eV on a Finnigan MAT SSQ 7000 spectrometer (England). Elemental analyses (C, H, and N) were performed using Elementar Vario EL-Germany Instrument, P was measured by spectrophotometric methods at the analytical laboratory of the National Research Center. The experimental values agreed well with the calculated ones. The reported yields are used upon pure materials isolated by column chromatography on silica gel 60 (Merck, Darmstadt, Germany).

Reaction of 2-Hydroxyisoindole-1,3(2*H*)dione (1) with Stabilized Phosphonium Ylides 2a–d

General Procedure. To a solution of 2-hydroxyisoindole **1** (0.326 g, 2 mmol) in dry toluene (20 mL), was added a solution of the methylenetriphenylphosphoranes **2a–d**,[34,35] (2 mmol) in dry toluene (30 mL) and the reaction mixture was refluxed for 3 h monitored by thin layer chromatography (TLC). The solvent was distilled off and the residue was

chromatographed on silica gel using petroleum ether 60–80 °C/acetone as eluent affording compounds **4a**–**d**, together with triphenylphosphane oxide (mp and mixed mp 151 °C).

2-Hydroxy-3-(2-oxopropylidene) isoindolin-1-one (4a)

Eluent: petroleum ether 60–80 °C/acetone (35:65, v/v). Yellow crystals; yield 70%; mp 103–105 °C. IR (KBr, ν cm^{-1}): 3245 (OH), 1791 (CO–CH_3), 1668 (C=O, isoindolone). ^{1}H NMR (500.14 MHz, $CDCl_3$, δ ppm): 2.62 (s, 3H, CH_3), 5.95 (s, 1H, CH), 7.45–7.65 (m, 4H, arom-H), 7.91 (OH, exchangeable with D_2O). ^{13}C NMR (125.76 MHz, $CDCl_3$, δ ppm): 30.0 (CH_3), 109.6 (CH), 157.5 (C=O, isoindolone), 197.5 (CO–CH_3). MS *m/z* (%) = 204 [(M+H), 100]. Anal. calcd. for $C_{11}H_9NO_3$ (203.06): C, 65.02; H, 4.46; N, 6.89%. Found: C, 65.10; H, 4.30; N, 6.56%.

2-Hydroxy-3-(2-oxo-2-phenylethylidene)isoindolin-1-one (4b)

Eluent: petroleum ether 60–80 °C/acetone (30:70, v/v). Yellow crystals; yield 73%; mp 146–148 °C. IR (KBr, ν cm^{-1}): 3201 (OH), 1658 (CO–Ph), 1612 (C=O, isoindoline). ^{1}H NMR (500.14 MHz, $CDCl_3$, δ ppm): 5.62 (s, 1H, CH), 7.40–8.00 (m, 9H, arom-H), 9.54 (OH, exchangeable with D_2O). MS, *m/z* (%) = 265 (M^+, 37.39), 160 [M^+−(CO–Ph), 30.41], 105 [(CO–Ph), 100]. Anal. calcd. for $C_{16}H_{11}NO_3$ (265.07): C, 72.45; H, 4.18; N, 5.28%. Found: C, 72.22; H, 4.02; N, 5.11%.

Methyl-2-(2-hydroxy-3-oxoisoindolin-1-ylidene)acetate (4c)

Eluent: petroleum ether 60–80 °C/acetone (40: 60, v/v). Yellow crystals; yield 69%; mp 174–176 °C. IR (KBr, ν cm^{-1}): 3210 (OH), 1790 (CO–OCH_3), 1665 (C=O, isoindoline). ^{1}H NMR (500.14 MHz, $CDCl_3$, δ ppm): 3.75 (s, 3H, OCH_3), 5.55 (s, 1H, CH), 7.65–7.86 (m, 4H, arom-H), 9.10 (s, 1H, OH, exchangeable with D_2O). ^{13}C NMR (125.76 MHz, $CDCl_3$, δ ppm): δ 51.8 (OCH_3), 102.5 (CH), 156.5 (C=O, isoindoline), 168.5 (CO–OCH_3). MS, *m/z* (%) = 219 (M^+, 5.40), 218 [M^+−(H), 4.97], 204 [M^+−(CH_3), 4.86], 202 [M^+−(OH), 8.52], 188 [M^+−(OCH_3), 5.11]. Anal. calcd. for $C_{11}H_9NO_4$ (219.19): C, 60.27; H, 4.14; N, 6.39%. Found: C, 60.10; H, 4.00; N, 6.26%.

Ethyl-2-(2-hydroxy-3-oxoisoindolin-1-ylidene)acetate (4d)

Eluent: petroleum ether 60–80 °C/acetone (60:40, v/v). Yellow crystals; yield 72%; mp 149–151 °C. IR (KBr, ν cm^{-1}): 3391 (OH), 2922 (CH_3), 2854 (CH_2), 1771 (CO–OC_2H_5), 1668 (C=O, isoindoline). ^{1}H NMR (500.14 MHz, $CDCl_3$, δ ppm): 1.25 (t, 3H, CH_2–CH_3), 4.20 (q, 2H, CH_2–CH_3), 5.55 (s, 1H, CH), 7.60–7.81 (m, 4H, arom-H), and 9.00 (s, 1H, OH, exchangeable with D_2O). ^{13}C NMR (125.76 MHz, $CDCl_3$, δ ppm): 14.1 (CH_3), 62.5 (CH_2), 106.5 (CH), 158.5 (C=O, isoindoline), 168.7 (CO–OC_2H_5). MS, *m/z* (%) = 232 [M^+−(H), 1.02], 205 [M^+−(CO), 1.27]. Anal. calcd. for $C_{12}H_{11}NO_4$ (233.07): C, 61.80; H, 4.75; N, 6.01%. Found: C, 61.55; H, 4.50; N, 6.00%.

Reaction of 2-Hydroxyisoindole-1,3(2*H*)dione (1), Isoindoline-1,3-dione (8) and Indane-1,3-dione (10) with Phosphacumulene 5a

General Procedure. To a solution of **1**, **8**, or **10** (1 mmol) in dry THF (20 mL), was added dropwise with stirring a solution of (*N*-phenyliminovinyldene)triphenylphosphorane (**5a**)[36] (0.754 g, 2 mmol). The reaction mixture was stirred at room temperature for 3 h in case of compound **1**, and for 4 h when compounds **8** or **10** was used (TLC), during which the color changed from yellow to deep orange. The solvent was removed under reduced pressure and the residue was chromatographed on silica gel using petroleum ether 60–80 °C/ethyl acetate or acetone as eluent affording compounds **7a**, **9a**, and **11a**. Triphenylphosphane oxide was also isolated from the reaction medium and identified (mp and mixed mp).

2,4-Bis(phenylimino)-3-[(triphenylphosphanylidene)cyclobutylidene)]-2-hydroxyisoindolin-1-one (7a)

Eluent: petroleum ether 60–80 °C/ethyl acetate (80:20, v/v). Yellow crystals; yield 65%; mp 211–213 °C. MS, *m/z* (%) = 361 [$M^+-(Ph_3P{=}O)$, 100]. Anal. calcd. for $C_{42}H_{30}N_3O_2P$ (639.21): C, 78.86; H, 4.73; N, 6.57; P, 4.84%. Found: C, 78.56; H, 4.48; N, 6.50; P, 4.53%.

3-[2,4-Bis(phenylimino)-3-(triphenyl-λ^5-phosphanylidene) cyclobutylidene]isoindolin-1-one (9a)

Eluent: petroleum ether 60–80 °C/acetone (70:30, v/v). Orange crystals; yield 69%; mp 227–229 °C. IR (KBr, ν cm^{-1}): 3197 (NH), 1674 (C=O), 1624 (C=N), 1565 (C=P), 1467 (P-phenyl). ^{1}H NMR (500.14 MHz, $CDCl_3$, δ ppm): 8.30 (s, 1H, NH, exchangeable with D_2O), 6.45–7.69 (m, 29H, arom-H). ^{13}C NMR (125.76 MHz, $CDCl_3$, δ ppm): 146.6 (d, $^1J_{CP}$ = 92.4 Hz, C=P), 149.6 (C=C–NH), 162.6 (C=N), 165.5 (C=O). ^{31}P NMR (202.4 MHz, $CDCl_3$, δ ppm): 15.2. MS, *m/z* (%) = 278 ($Ph_3P{=}O$, 100), 345 [$M^+-(Ph_3P{=}O)$, 100]. Anal. calcd. for $C_{42}H_{30}N_3OP$ (623.21): C, 80.88; H, 4.85; N, 6.74; P, 4.97%. Found: C, 80.77; H, 4.53; N, 6.53; P, 4.76%.

3-[2,4-Bis(phenylimino)-3-(triphenyl-λ^{5}phosphanylidene) cyclobutylidene]-2,3-dihydro-1H-iden-1-one (11a)

Eluent: petroleum ether 60–80 °C/acetone (60:40, v/v). Yellow crystals; yield 66%; mp 263–265 °C. IR (KBr, ν cm^{-1}): 1720 (C=O), 1622 (C=N), 1566(C=P), 1446 (P-phenyl). ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 2.50 (s, 2H, CH_2), 6.62–7.62 (m, 29H, arom-H). ^{13}C NMR (125.76 MHz, $CDCl_3$, δ ppm): 42.5 (CH_2), 148.2 (d, $^1J_{CP}$ = 93.5 Hz, C=P), 169.5 (C=N), 189.0 (C=O). ^{31}P NMR (202.4 MHz, $CDCl_3$, δ ppm): −4.[22] Anal. calcd for $C_{43}H_{31}N_2OP$ (622.22): C, 82.94; H, 5.02; N, 4.50; P, 4.97%. Found C, 82.73; H, 4.85; N, 4.30; P, 4.53%.

Reaction of 2-Hydroxyisoindole-1,3(2*H*)dione (1), Isoindoline-1,3-dione (8) and Indane-1,3-dione (10) with Phosphacumulene 5b

General Procedure. To a solution of **1**, **8**, or **10** (1 mmol) in dry toluene (20 mL) was added a solution of (2-oxovinylidene)triphenylphosphorane **(5b)**[37] (0.604 g, 2 mmol) in

dry toluene (30 mL). The reaction mixture was refluxed for 5 h when compound **1** was used and for 6 h in case of **8** or **10** (TLC). Toluene had been distilled off under reduced pressure. The residue was chromatographed on silica gel using petroleum ether 60–80 °C/acetone as eluent, affording **7b**, **9b**, and **11b**, and triphenylphosphane oxide was also isolated and identified (mp and mixed mp).

2-(2-Hydroxy-3-oxo-2,3-dihydro-1*H*-isoindol-1-ylidene)-4-(triphenyl-λ^5-phosphanylidene)cyclobutane-1,3-dione (7b)

Eluent: petroleum ether 60–80 °C/acetone (80:20, v/v). Yellow crystals; yield 62% mp 163–165 °C. IR: (KBr, ν cm^{-1}): 3345 (OH), 1724 (C=O, cyclic), 1682 (C=O, isoindoline), 1438 (P-phenyl). ^{1}H NMR (500.14 MHz, $CDCl_3$, δ ppm): 6.86–7.52 (m, 19H, arom-H), 10.21 (s, 1H, OH, exchangeable with D_2O). ^{31}P NMR (202.4 MHz, $CDCl_3$, δ ppm) = 19.7. MS, *m/z* (%) = 278 (Ph_3P=O, 100), 199 [M$^+$−(Ph_3P + CO) 24.59]. Anal. calcd. for $C_{30}H_{20}NO_4P$ (489.11): C, 73.62;H, 4.12; N, 2.86; P, 6.34%. Found: C, 73.50; H, 4.00; N, 2.74; P, 6.22%.

2-(3-Oxo-2,3-dihydro-1*H*-isoindol-1-ylidene)-4-(triphenyl-λ^5-phosphanyli-dene)cyclobutane-1,3-dione (9b)

Eluent: petroleum ether 60–80 °C/acetone (70:30, v/v). Yellow crystals; yield 65%; mp 178–180 °C. IR (KBr, ν cm^{-1}): 3048 (NH), 1720 (C=O, cyclic), 1659 (C=O, isoindole), 1576 (C=P), 1436 (P-phenyl). ^{1}H NMR (500.14 MHz, $CDCl_3$, δ ppm): 7.33–7.80 (m, 19H, arom-H), 8.13 (s, 1H, NH, changed with D_2O). ^{13}C NMR (125.76 MHz, $CDCl_3$, δ ppm): 142.6 (d, $^1J_{CP}$ = 95.3 Hz, C=P), 168.6 (C=C–NH), 165.5 (C=O, isoindole), 188.4 (C=O, cyclic). ^{31}P NMR (202.4 MHz, $CDCl_3$, δ ppm): 15.7. MS, *m/z* (%) = 278 (Ph_3P=O, 100), 183 [M$^+$−(Ph_3P + CO), 12.81]. Anal. calcd for $C_{30}H_{20}NO_3P$ (473.12): C, 76.10; H, 4.26; N, 2.96; P, 6.54%. Found: C, 76.01; H, 4.15; N, 2.40; P, 6.35%.

2-(3-Oxo-2,3-dihydro-1*H*-inden-1-ylidene)-4-(triphenyl-λ^5-phosphanylidene)cyclobutane-1,3-dione (11b)

Eluent: petroleum ether 60–80 °C/acetone (70:30, v/v); orange crystals; mp 220 °C; yield 72%. IR (KBr, ν cm^{-1}): 2848 (CH_2), 1723 (C=O, cyclic), 1687 (C=O, indene), and 1436 (P-phenyl). ^{1}H NMR ($CDCl_3$, δ ppm): 2.40 (s, 2H, CH_2), 6.61–7.61 (m, 19H, arom-H). ^{13}C NMR (125.76 MHz, $CDCl_3$, δ ppm): 48.3 (CH_2), 136.6 (C–C=O, indene), 137.5 (C–C=O, cyclic), 145.5 (C=C–C=O), 148.3 (d, $^1J_{CP}$ = 96.8, Hz, C=P), 172.2 (C–CH_2), 189.3 (C=O, cyclic), 194.5 (C=O, indene). ^{31}P NMR (202.4 MHz, $CDCl_3$, δ ppm): 14.8. MS, *m/z* (%) = 278 (Ph_3P=O, 100), 182 [M$^+$−(Ph_3P + CO), 14.62]. Anal. calcd. for $C_{31}H_{21}O_3P$ (472.12): C, 78.81; H, 4.48; P, 6.56%. Found: C, 78.61; H, 4. 21; P, 6.3%.

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