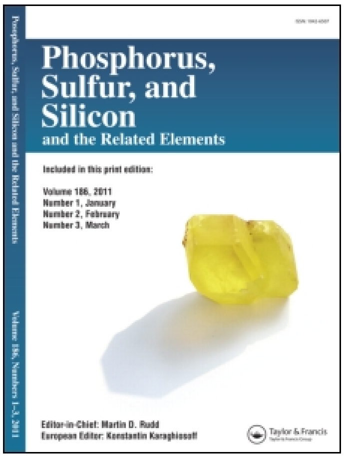

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Soliman, Fouad M. and Said, Medhat M.(1991) 'CHEMISTRY OF PHOSPHORUS YLIDES 10[1] REACTION WITH PHOSPHACUMULENES IV. SYNTHESIS OF PYRAN, PHOSPHORANYLIDENE, OXAPHOSPHORIN AND OXAZAPHOSPHORIN FROM THE REACTION OF 1,3-DIOXO-$\Delta^{2,\alpha}$-INDANMALONONITRILE WITH PHOSPHORANES AND IMINOPHOSPHORANES', Phosphorus, Sulfur, and Silicon and the Related Elements, 61: 3, 335 — 340

To link to this Article: DOI: 10.1080/10426509108036815

URL: http://dx.doi.org/10.1080/10426509108036815

Phosphorus, Sulfur, and Silicon, 1991, Vol. 61, pp. 335–340
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CHEMISTRY OF PHOSPHORUS YLIDES 10[1] REACTION WITH PHOSPHACUMULENES IV. SYNTHESIS OF PYRAN, PHOSPHORANYLIDENE, OXAPHOSPHORIN AND OXAZAPHOSPHORIN FROM THE REACTION OF 1,3-DIOXO-$\Delta^{2,\alpha}$-INDANMALONONITRILE WITH PHOSPHORANES AND IMINOPHOSPHORANES

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(Received December 11, 1990; in final form January 23, 1991)

Dedicated to professor Dr. Hans Jürgen Bestmann on the Occasion of his 65th birthday.

1,3-Dioxo-$\Delta^{2,\alpha}$-indanmalononitrile (**1**) reacts with the active ketenylidene-(**2a**) and thioketenylidenetriphenyl phosphorane (**2b**) to give the corresponding pyrans 3 (X=O or S). The reaction of pyran **3** with *p*-nitrobenzaldehyde proceeds according to the Wittig reaction to give the respective ethylenes **4a, b**. On the other hand, phosphoranylidenes **7a–e** were isolated from the reaction of stable phosphoranes **5a–e** with the dioxoindanmalononitrile **1**. Moreover, the oxaphosphorin **9** and oxazaphosphorin **11**, were prepared from the reaction of compound **1**, with the phosphorane **8**, and the iminophosphorane **10**, respectively. Structures of the new compounds were assigned according to consistent analytical and spectroscopic measurements.

Key words: Dioxoindanmalononitrile; phosphoranes; pyrans; phosphoranylidenes; oxaphosphorin; oxazaphosphorin.

INTRODUCTION

The cumulated phosphonium ylides form a unique group within the ylides, which have been used by Bestmann[2] as very versatile synthones in organic synthesis. Therefore, we have now studied the reaction of 1,3-dioxo-$\Delta^{2,\alpha}$-indanmalononitrile (**1**), with the active phosphacumulenes (**2a, b**). A comparative study on the reactivity of compound **1**, towards stable ylide-phosphoranes (**5a–e, 8**) and the iminophosphorane **10** is undertaken, too.

RESULTS AND DISCUSSION

We have found that 1,3-dioxo-$\Delta^{2,\alpha}$-indanmalononitrile (**1**) reacts with ketenylidenetriphenylphosphorane (**2a**), in dry tetrahydrofuran at room temperature for 6 hours by [4 + 2] cycloaddition to the corresponding pyran which can be represented by the resonance structures, namely, 2,3-dihydro-2,5-dioxo-3(triphenylphosphoranylidene) indeno [1,2-**b**] pyran-4,4(2H) dicarbonitrile **3a** (X=O), and (4,4-dicyano-4,5-dihydro-2-hydroxy-5-oxoindeno[1,2-**b**] pyran-3-yl) triphenylphosphonium hydroxide, inner salt **3b** (X=O). Satisfactory elemental microanalysis and molecular weight determination (MS) confirm the proposed structure **3** (X=O). Its IR spectrum showed strong absorption bands at 2200 cm^{-1} (C≡N), 1710 and 1680 cm^{-1} (C=O), 1635 (P=C)[3] and 1440 cm^{-1} (*P*-aryl).[4] In the ^{31}P-NMR spectrum of **3** (X=O), a signal at δ +22.29 ppm was observed which supports structure **3** and excludes 4-membered ring structure by [2 + 2]-cycloaddition which would have a signal form +5 till −5 ppm. In the MS of **3** (X=O) the m/e is 510 (M^+).

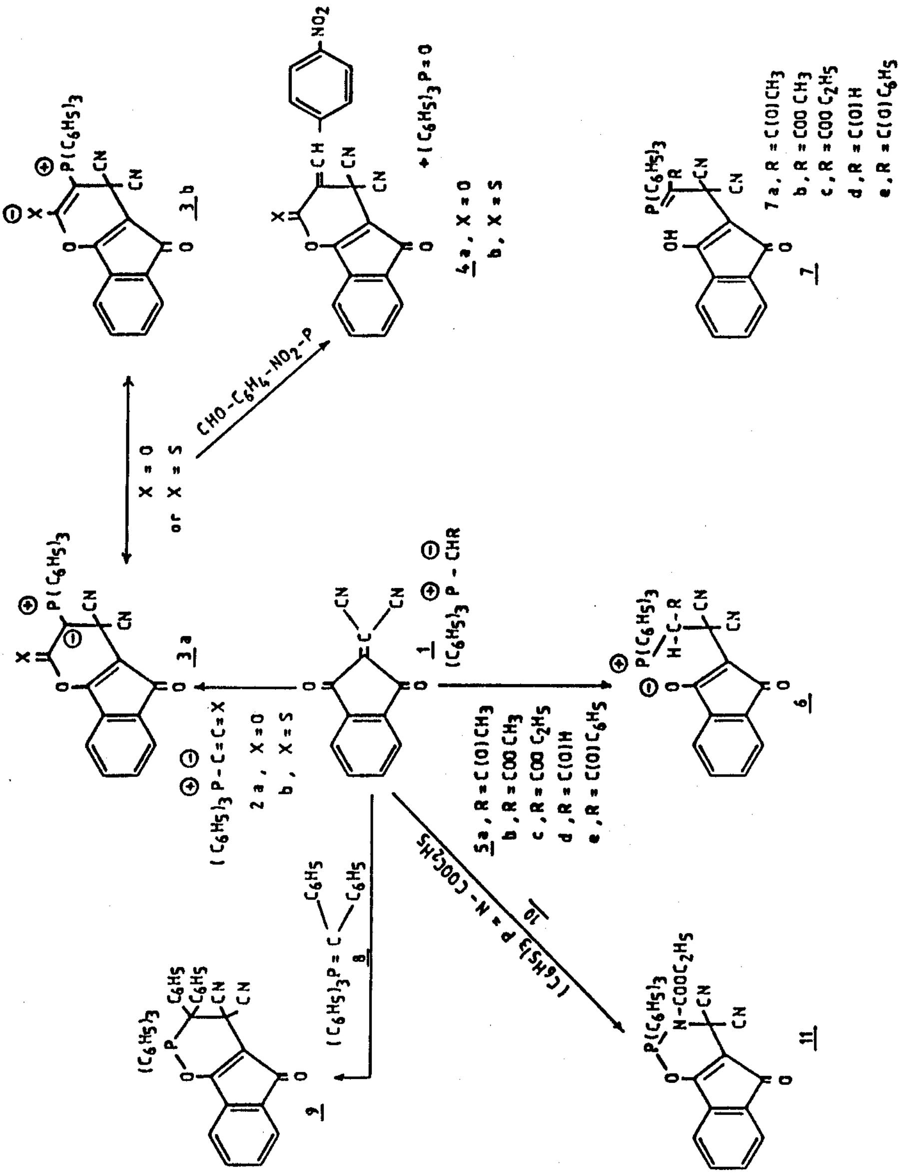
The reaction of the dioxoindanmalononitrile **1** with thioketenylidenetriphenylphosphorane **2b** was also conducted under the same experimental condition. The new 2,3-dihydro-5-oxo-2-thio-3-(triphenylphosphoranylidene) indeno[1,2-**b**], pyran-4,4 (5**H**)-dicarbonitrile **3** (X=S), was isolated in satisfactory yield. Evidences for structure **3** (X=S) are:

(a) It gave correct elemental analysis and the molecular weight determination (MS) corresponded to $C_{32}H_{19}N_2O_2PS$.
(b) The C=S absorption band[4] was present at 1240 cm^{-1} in the IR spectrum of **3** (X=S). Besides, absorption bands due to C≡N (2200), C=O (1700), P=C (1640); *P*-aryl (1440), were observed too. ^{31}P-NMR +21.18 ppm and m/e = 526 (M^+).

When the Wittig reaction[6] was carried out with the pyran compound **3** (X=O) and/or **3** (X=S), using *p*-nitrobenzaldehyde, the new exocyclic olefins, namely, 2,3-dihydro-3-(*p*-nitrobenzylidene)-2,5-dioxoindeno[1,2-**b**] pyran-4.4 (5**H**)-dicarbonitrile **4a** and 2,3-dihydro-3-(*p*-nitrobenzylidene)-5-oxo-2-thioxoindeno [1,2-**b**]-pyran-4.4 (5**H**)-dicarbonitrile **4b**, were isolated respectively together with triphenylphosphine oxide. The structure of the new compounds **4a** and **4b** is assignable from their analysis, IR and mass spectral data. The IR of **4a**, shows bands at 2200 cm^{-1} (C≡N), 1710 and 1675 cm^{-1} (C=O). Moreover, the mass spectrum of **4a** shows the ion peak at m/e 383 (M^+). On the other hand, the IR spectrum of **4b**, shows bands at 2200 cm^{-1} (C≡N), 1710 cm^{-1} (C=O) and 1250 cm^{-1} (C=S). In the MS of **4b** the m/e = 399 (M^+).

We have also found that the dioxoindanmalononitrile **1** reacts with the stabilized methylenetriphenylphosphoranes, namely, acetyl-(**5a**), methoxycarbonyl-(**5b**), ethoxycarbonyl-(**5c**), formyl-(**5d**) and benzoylmethylenetriphenyl phosphorane (**5e**), in THF at room temperature to give the brown crystalline phosphoranylidenes **7a–e**. Structure **7** was confirmed by compatible elemental analysis and spectroscopic data. The IR spectrum of 3-hydroxy-1-oxo-α-[1-(triphenyl phosphoranylidene) acetonyl] indene-2-malononitrile (**7a**), taken as a representative example revealed the presence of strong absorption bands at 3400 cm^{-1} (OH), 2200 (CN), strong band at 1720 cm^{-1} ($COCH_3$ and CO indene), 1630 cm^{-1} (P=C), 1435 cm^{-1} (*P*-aryl). The PMR spectrum of **7a**, showed signals at 1.6 (3H, CH_3, *s*), the OH proton showed a singlet (exchangeable with D_2O) at 6.1, while the aromatic protons appeared as a multiplet at 7.6 ppm. A signal at δ +19.27 was observed in the ^{31}P-NMR of **7a**, which supports the phosphoranylidene structure.[7]

Diphenylmethylenetriphenylphosphorane (**8**) reacted with the dioxomalononitrile **1**, in ethanol in the presence of sodium ethoxide, at room temperature for three hours, to give the corresponding 2,2,2,3-tetrahydro-5-oxo-2,2,2,3,3-pentaphenylindeno [2,1-e]-1,2-oxaphosphorin-4,4 [5H]-dicarbonitrile **9**. The elemental


3a
3b
X = O
or X = S
CHO-C6H4-NO2-p
4a, X = O
b, X = S
+ (C6H5)3P=O
(C6H5)3P-C=C=X
2a, X = O
b, X = S
1
(C6H5)3P - CHR
5a, R = C(O)CH3
b, R = COOCH3
c, R = COOC2H5
d, R = C(O)H
e, R = C(O)C6H5
6
7
7a, R = C(O)CH3
b, R = COOCH3
c, R = COOC2H5
d, R = C(O)H
e, R = C(O)C6H5
(C6H5)3P = C(C6H5)2
8
9
(C6H5)3P = N-COOC2H5
10
11

microanalysis, IR, ^1H- and ^{31}P-NMR data agree with structure **9**. A signal at δ = +27.67 ppm was observed which is in good accord with oxaphosphorins.[8]

Iminophosphoranes are basic compounds like methylene phosphoranes and their reactions are often analogous. The reactivity of the phosphinimine results from the polarity of the P—N bond, which is influenced by the substituents, particularly on the nitrogen atom. We have found that the reaction of ethoxycarbonyltriphenyl phosphinimine (**10**) with the dioxoindanmalononitrile (**1**), was completed when the reactants were stirred in dry THF for six hours. The product was formulated as ethyl 4,4-dicyano-2,2,4,5-tetrahydro-5-oxo-2,2,2-triphenylindeno [2,1-**e**]-1,3,2-oxaphosphorine-3 (2H) carboxylate (**11**) for the following reasons. Its microanalytical data agree with **11**. Moreover, its IR spectrum showed strong absorption bands at 2200 cm^{-1} (CN), 1690 (CO indene) and (CO ester) and 1435 *P*-aryl. In the ^1H NMR of **11** signals at δ 1.2 (3H, CH_3, *t*), 3.5 (2H, CH_2, *q*) and 7.6 (19H, aromatics, *m*), appeared and it showed a positive chemical shift (δ +36.64) in the ^{31}P-NMR which supports structure **11**.

CONCLUSION

From the present investigation it can be concluded that the phosphoranes attack the dioxoindanmalononitrile (**1**) at the α,β-unsaturated system in a different manner. Although the initial step is nucleophilic attack by the carbanion centre in the ylides to the electron deficient center in **1**, the consequences of the initial step vary markedly according to the structure of the phosphorane. In case of the reaction of the reactive cumulated phosphonium ylids, ketenylidene-(**2a**) and thioketenylidenetriphenylphosphorane (**2b**), with compound **1**, the pyran **3** (X=O) and its thioanalogue **3** (X=S) were obtained. On the other hand, the *R* moiety in the stabilized phosphoranes (**5**), which is electron withdrawing in nature stabilizes the formation of phosphoranylidenes (**7**), via migration of the α proton of the dipolar adduct like **6**, to the electron rich center of the molecule. But diphenylmethylenetriphenylphosphorane (**8**) afforded the cyclic oxaphosphorin (**9**) on reaction with the dioxoindanmalononitrile (**1**). Moreover, the oxazaphosphorin (**11**) was produced from the reaction of compound **1** with the iminophosphorane (**10**). These processes can be considered as a new and simple route for the preparation of different ring systems, especially the thiopyran (**3**, X=S) which can not be obtained by other conventional methods.

EXPERIMENTAL

All melting points are uncorrected. Solvents were dried by standard technique. All reactions were carried out under N_2 atmosphere. The IR spectra were measured in KBr, on a Carl Zeiss Infracord Spectrometer Model UR 10. The ^1H-NMR spectra were run in $CDCl_3$, at 90 MHz on a Varian Spectrometer using TMS as an internal reference. ^{31}P-NMR spectra were performed on Spectrometer JNM-PS 100 Jeol Tokio in $CDCl_3$, using H_3PO_4 as external standard, MS were carried at 70 ev on Karatos equipment provided with data system. Elemental analysis: Microanalysis Lab., National Research Centre, Cairo.

2,3-Dihydro-2,5-dioxo-3-(triphenylphosphoranylidene) indeno [1,2-b]pyran-4,4(5H)-dicarbonitrile 3(X=O). To a solution of the yellow 1,3-dioxo $\Delta^{2,\alpha}$-indanmalononitrile (**1**)[9] (2.08 g, 0.01 mol) in 50 ml tetrahydrofuran, was added drop by drop with stirring at room temperature (25°C), a solution of ketenylidenetriphenyl phosphorane (**2a**)[10] (3.3 g, 0.011 mol) in 50 ml THF. The reaction mixture was stirred for six hours, during which the color changed from yellow to deep red. After THF was distilled under reduced pressure, the residue was triturated with ether, filtered and crystallized from chloroform/pet.ether (60–80°) to give **3** (X=O), as violet crystals, m.p. 160°C (decomp.), (4.59 g, 90%). Calc. for $C_{32}H_{19}N_2O_3P$:C, 75.29; H, 3.72; N, 5.49; P, 6.08. Found: C, 75.08; H, 3.75; N, 5.69; P, 6.37.

2,3-Dihydro-5-oxo-2-thio-3-(triphenylphosphoranylidene)indeno [1,2-b] pyran-4,4(5H)-dicarbonitrile **3** (X=S), was isolated from the reaction of the dioxoindanmalononitrile (**1**) (2.08 g, 0.01 mol) and thioketenylidenetriphenyl phosphorane (**2b**)[10] (3.5 g, 0.011 mol), as violet crystals m.p. 145°C (decomp.), from chloroform/pet. ether (60–80°C) (4.47 g, 85%). Calc. for $C_{32}H_{19}N_2O_2PS$: C, 73.00; H, 3.61; N, 5.49; P, 6.08; S, 6.08. Found: C, 72.91; H, 3.75; N, 5.18; P, 5.87; S, 6.34.

2,3-Dihydro-3-(p-nitrobenzylidene)-2,5-dioxoindeno-[1,2-b] pyran-4,4(5H)-dicarbonitrile (**4a**). A mixture of the phosphoranylidene **3** (X=O) (5.1 g, 0.01 mol) and *p*-nitrobenzaldehyde (1.7 g, 0.011 mol) and toluene (50 ml) was refluxed for 24 hours. Toluene was distilled off and the residue was crystallized from benzene to give **4a** as brown crystals m.p. 190°C, (3.0 g, 79%). Calc. for $C_{21}H_9N_3O_5$: C, 65.79; H, 2.34; N, 10.96. Found: C, 65.30; H, 2.24; N, 10.70.

The benzene filtrate afforded upon concentration and addition of *n*-hexane a colorless precipitate, which upon recrystallization gave triphenylphosphine oxide, m.p. and mixed m.p. 151°C (2.0 g, 75%).

In a similar manner, 2,3-dihydro-3(*P*-nitrobenzylidene)-5-oxo-2-thioxoindeno[1,2-**b**]pyran-4,4 (5H)-dicarbonitrile (**4b**) was obtained from the reaction of *p*-nitrobenzaldehyde (1.7 g, 0.011 mol) and the thiophosphoranylidene **3** (X=S) (5.22 g, 0.01 mol), as brown crystals, m.p. 210°C from benzene (3.0 g, 75%), Calc. for $C_{21}H_9N_3O_4S$: C, 63.16; H, 2.25; N, 10.52; S, 8.02. Found: C, 63.3; H, 2.00; N, 10.32; S, 7.89.

Reaction of 1,3-oxo-$\Delta^{2,\alpha}$-indanmalononitrile (1) with Wittig reagents (**5a–e**), *General procedure.* A solution of the Wittig reagents (**5a–e**) (0.01 mol) in 30 ml of THF was added dropwise while stirring at room temperature to a solution of the dioxoindanmalononitrile (**1**) (0.01 mol) in 30 ml THF. The reaction mixture was left for 12 hours during which it turned to a red solution. After THF was distilled under reduced pressure, the residue was treated with dry ether, filtered and crystallized from benzene/pet.ether 40–60°C. to give the triphenylphosphoranylidene products (**7a–e**).

3-Hydroxy-1-oxo-α[1-(triphenylphosphanylidene)acetonyl]indene-2-malononitrile (**7a**) was obtained from the reaction of acetylmethylentriphenylphosphorane (**5a**)[12] and the indanmalononitrile (**1**), as brown crystals, m.p. 180°C decomp. (93%). Calc. for $C_{33}H_{23}N_2O_3P$: C, 75.28; H, 4.37; N, 5.32; P, 5.89. Found: C, 72.25; H, 4.30; N, 5.50; P, 5.69.

Methyl-β,β-dicyano-3-hydroxy-1-oxo-α-(triphenylphosphoranylidene)indene-2-propionate (**7b**) was similarly obtained from methoxycarbonylmethylenetriphenylphosphorane (**5b**)[13] and the indanmalononitrile (**1**), as yellowish brown crystals, m.p. 115°C decomp. (78%) Calc. for $C_{33}H_{23}N_2O_4P$: C, 73.06; H, 4.24; N, 5.17; P, 5.72. Found: C, 73.20; H, 4.41; N, 4.99; P, 5.86, IR (cm^{-1}): Bands at 3420 (OH), 2200 (CN), strong band at 1730 [C(O)OCH_3 and C(O) indene], 1620 (P=C), 1440 (*P*-aryl). ^{1}H-NMR (δ): Signals at 3.5 (3H, OCH_3, *s*), 6.15 (OH) and 7.5 (19H, aromatics, *m*). ^{31}P NMR: δ +21.36.

Ethyl β,β-dicyano-3-hydroxy-1-oxo-α-(triphenylphosphoranylidene) indene-2-propionate (**7c**) was isolated from the reaction of ethoxycarbonylmethylenetriphenylphosphorane (**5c**)[13] and the dioxoindanmalononitrile (**1**), as pale brown crystals, m.p. 110°C decomp. (75%). Calc. for $C_{34}H_{25}N_2O_4P$: C, 73.38; H, 4.49; N, 5.03; P, 5.57. Found C, 73.41; H, 4.33; N, 4.95; P, 5.76. IR (cm^{-1}): 3415 (OH), 2200 (CN), 1725 [C(O)OC_2H_5 and C(O) indene] 1620 (P=C), 1440 (*P*-aryl). ^{1}H-NMR (δ): 1.2 (3H, ethoxy CH_3, *t*), 3.5 (2H, ethoxy-CH_2, *q*), 6.1 (OH), 7.5 (19 H, aromatics, *m*).

α-[Formyl(triphenylphosphoranylidene)methyl]-3-hydroxy-1-oxo-indene-2-malononitrile (**7d**) was prepared from the reaction of formyl methylenetriphenylphosphorane (**5d**)[14] and the indanmalononitrile (**1**), as violet crystals m.p. 205° (70%). Calc. for $C_{32}H_{21}N_2O_3P$: C, 75.00; H, 4.10; N, 5.46; P, 6.05. Found C, 75.20; H, 4.00; N, 5.26; P, 6.06. IR (cm^{-1}): 3420 (OH), 2200 (CN), 1735 (CHO), 1710 (CO indene), 1620 (P=C), 1440 (*P*-aryl). ^{31}P NMR: δ +22.03.

3-Hydroxy-1-oxo-α-[α-(triphenylphosphoranylidene)phenacyl]indene-2-malononitrile (**7e**) was synthesized from benzoylmethylenetriphenylphosphorane (**5e**)[12] and indanmalononitrile (**1**), as pale brown crystals, m.p. 185°C (72%). Calc. for $C_{33}H_{25}N_2O_3P$: C, 77.55; H, 4.25; N, 4.76; P, 5.27. Found: C, 77.85; H, 4.36; N, 4.67; P, 5.43. IR (cm^{-1}): 3420 (OH), 2200 (CN), 1730 (COC_6H_5 and CO indene), 1620 (P=C), 1440 (*P*-aryl). ^{31}P NMR: δ +22.032.

2,2,2,3-Tetrahydro-5-oxo-2,2,2,3,3-pentaphenylindeno [2.1–e]-1,2-oxaphosphorin-4,4 (5H)-dicarbonitrile (**9**). A solution of diphenylmethylenetriphenylphosphonium chloride (**8**)[15] (4.63 g, 0.01 mol) in 20 ml of absolute ethanol was treated with 20 ml of a 0.01 M solution of sodium ethoxide in ethanol with continuous stirring, where the orange color of the phosphorane appeared immediately. The phosphorane solution was then added to a solution of the dioxoindanmalononitrile (**1**) (2g, 0.01 mol) in 30 ml absolute ethanol and the reaction mixture was stirred for one hour at 25°C. Ethanol was distilled under reduced pressure and the remaining precipitate was extracted with dry benzene. After the benzene extract has been concentrated in vacuo, red crystals of the oxaphosphorin **9** precipitated, which were recrystallized from chloroform/pet. ether (60–80°C), m.p. 160°C (70%). Calc. for $C_{43}H_{29}N_2O_2P$: C, 81.13; H, 4.56; N, 4.40; P, 4.87. Found: C, 80.99; H, 4.65; N, 4.60; P, 4.90.

Ethyl 4,4-dicyano-2,2,4,5-tetrahydro-5-oxo-2,2,2-triphenyl-indeno [2.1–e]-1,3,2-oxazaphosphorine-3 (2H)-carboxylate (**11**). A solution of ethoxycarbonyltriphenylphosphinimine (**10**)[16] (3.5 g, 0.011 mol) in 30 ml THF, was added dropwise under stirring to a solution of the dioxoindanmalononitrile **1** (2 g, 0.01 mol) in 30 ml THF. The reaction mixture was kept at room temperature (30°C) for six hours, during which the color changed to dark brown then left in the refrigerator (7°C) for 12 hours. The precipitate that formed was washed with dry ether and crystallized from chloroform/pt.ether (60–80°C) to give the oxazaphosphorine **11**, as orange crystals m.p. 237°C decomp. (4.4 g, 80%) Calc. for $C_{33}H_{24}N_3O_4P$: C, 71.09; H, 4.03; N, 7.54; P, 5.56. Found: C, 71.08; H, 4.41; N, 7.80; P, 5.60.

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