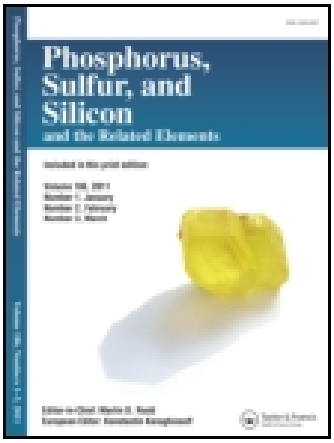


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# Chemistry of Phosphorus Ylides. Part 34 Synthesis of Chromenone Phosphanylidene and Cyclobutylidene Derivatives

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# CHEMISTRY OF PHOSPHORUS YLIDES, PART 34: SYNTHESIS OF CHROMENONE PHOSPHANYLIDENE AND CYCLOBUTYLIDENE DERIVATIVES

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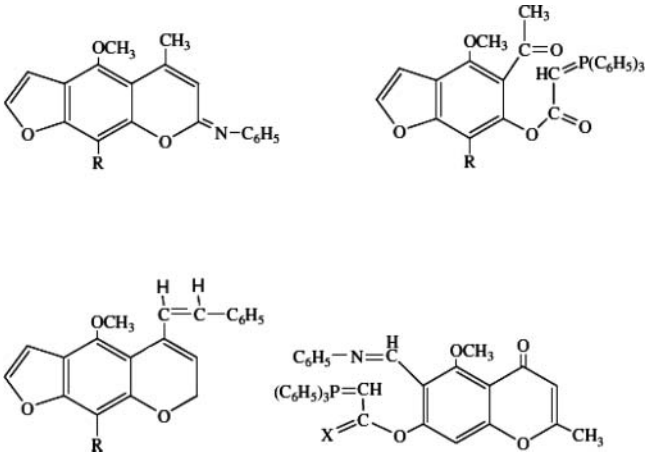
## GRAPHICAL ABSTRACT




**Abstract** *The reaction of nucleophilic phosphacumulene ylides with visnaginone and khellinone afforded the corresponding phosphanylidene and furochromene derivatives. Moreover, pyranochromenes were obtained from the reaction of chromene carbaldehydes with phosphacumulenes. On the other hand, the phosphanylidene-cyclobutylidenes and their dimers were produced from the reaction of furochromene carbaldehydes with the same phosphonium reagents.*

**Keywords** Cyclobutylidenes; furochromenes; Phosphacumulene ylides; phosphanylidenes; pyranochromenes

## INTRODUCTION

Visnagin and khellin are natural linear furochromenes that can be isolated from Ammi visnaga L.,[1] which are perennial herbaceous plants that grow wild in many Eastern

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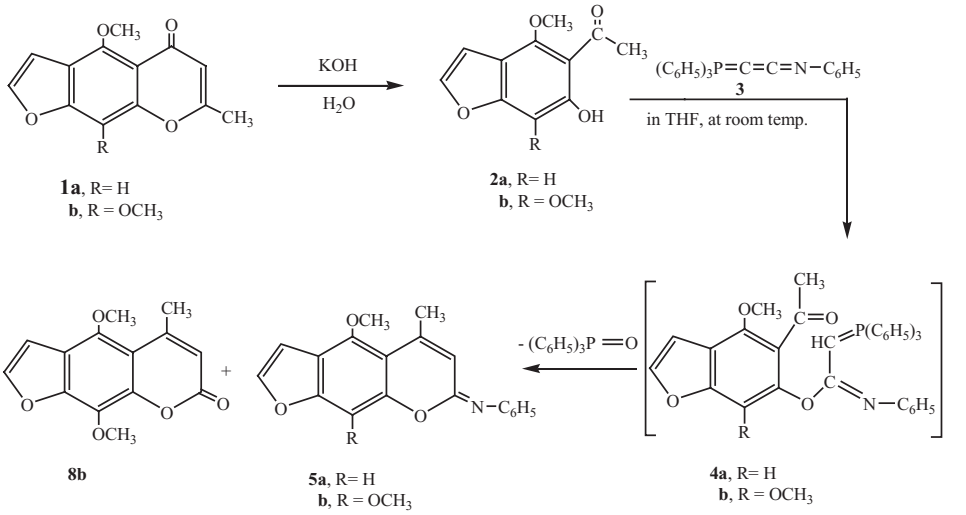
Mediterranean countries.[2] They have antispasmodic properties and are used in the treatment of angina pectoris.[3] Moreover, the anticancer activities of these naturally occurring furochromones have been reported.[4,5] On the basis of these findings, the present work was aimed to synthesize a new group of furochromones incorporating different heterocycle, carbocycle, and phosphorane moieties. We expected the resulting compounds to have higher activities and lower side effects acting as antitumor agents.

## RESULTS AND DISCUSSION

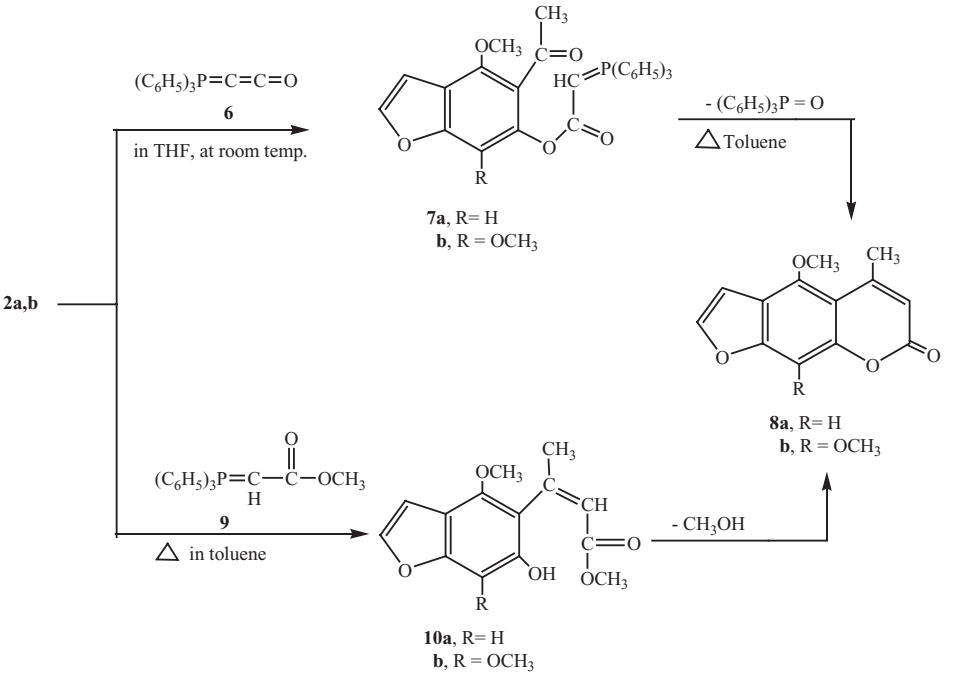
Owing to our interest in the synthesis of analogues of naturally occurring compounds containing phosphorane, heterocyclic, and carbocyclic moieties,[6–10] we investigated the reaction of active nucleophilic phosphacumulene ylides with benzofuranes and chromones. The benzofuranes 1-(6-hydroxy-4-methoxybenzofuran-5-yl) ethanone (visnaginone) (**2a**) and 1-(6-hydroxy-4,7-dimethoxybenzofuran-5-yl) ethanone (khellinone) (**2b**) were obtained by aqueous alkaline hydrolysis of visnagin (**1a**) and khellin (**1b**), respectively.[11] We have found that the reaction of visnaginone (**2a**) with one equivalent of (*N*-phenyliminovinylidene)triphenylphosphorane (**3**) proceeds in dry tetrahydrofuran (THF) at room temperature for 8 h to give *N*-(4-methoxy-5-methyl-*7H*-furo[3,2-*g*]chromen-7-ylidene)benzenamine (**5a**) together with triphenylphosphine oxide (TPPO). Carrying out the same reaction using two equivalents of the active phosphacumulene **3** led to the formation of the same product **5a**. The phosphacumulene **3** is added to the phenolic OH group rather than the acetyl carbonyl group of **2a** to give first the intermediate ylide **4a**, which cyclizes by intramolecular *Wittig* reaction with the formation of the furochromeneylidene **5a** along with TPPO. The structure of compound **5a** was established on the basis of IR, $^{1}$H, $^{13}$C NMR, and mass spectral data. The mass spectrum of compound **5a** showed the molecular ion peak at m/z = 305 ($M^+$, 35.5%). The $^{1}$H NMR spectrum of **5a** showed signals at $\delta = 2.55$ ($CH_3$) as a doublet ($J_{HH} = 2.5$ Hz) due to allylic coupling with the vinyl proton at C-6, which appeared at $\delta = 6.09$. The NMR signal for the $OCH_3$ protons was found at $\delta = 4.09$, and the furan ring protons gave two doublets (each with $J_{HH} = 2.30$ Hz) at $\delta = 6.98$ (3-H) and at $\delta = 7.57$ (2-H). The signal at $\delta = 7.14$ was attributed to the proton at C-9. Khellinone (**2b**) was found to react with phosphorane **3** in THF at room temperature during 10 h to give TPPO alongwith a mixture of two products, compounds **5b** and **8b**. The first main product was identified as *N*-(4,9-dimethoxy-5-methyl-*7H*-furo[3,2-*g*]chromen-7-ylidene) benzenamine (**5b**), and the second minor product was identified as 4,9-dimethoxy-5-methyl-*7H*-furo[3,2-*g*]chromen-7-one (**8b**). Compound **8b** was obtained by partial hydrolysis of **5b**. When compound **5b** was boiled in toluene for 3 h, compound **8b** and traces of **5b** were isolated (Scheme 1).

The reaction of (2-oxovinylidene)triphenylphosphorane (**6**) with **2a** and **2b** was also investigated. We have found that the reaction proceeds in THF at room temperature and is complete within 8 h in the case of **2a** and within 12 h in the case of **2b** to give (triphenyl-$\lambda^5$-phosphanylidene)acetic acid 5-acetyl-4-methoxy-benzofuran-6-yl ester (**7a**) and (triphenyl-$\lambda^5$-phosphanylidene)acetic acid 5-acetyl-4,7-dimethoxybenzofuran-6-yl ester (**7b**), respectively. The phosphanylidene **7a** shows a peak in the mass spectrum at m/z = 508 ($M^+$, 25.3%) and a signal in the $^{31}$P NMR spectrum at $\delta = 17.4$ ppm, which supports a phosphorane structure.[12–14] When the phosphoranes **7a** and **7b** are boiled in toluene, intramolecular *Wittig* reaction occurs with the formation of 4-methoxy-5-methyl-*7H*-furo[3,2-*g*]chromen-7-one (**8a**) and 4,9-dimethoxy-5-methyl-*7H*-furo[3,2-*g*]chromen-7-one (**8b**), respectively, together with TPPO. It was reported[15] that the reaction of a stabilized phosphonium ylide,




**Scheme 1**

carbmethoxymethylenetriphenylphosphorane (**9**), with compounds **2a** and **2b** affords the chromenones **8a** and **8b**, respectively. In this case the stabilized phosphonium ylide **9** reacts with the acetyl carbonyl group rather than with the OH group to give the intermediate compounds **10a**,**b**, which are lactonized to give compounds **8a**,**b** with elimination of methanol (Scheme 2).



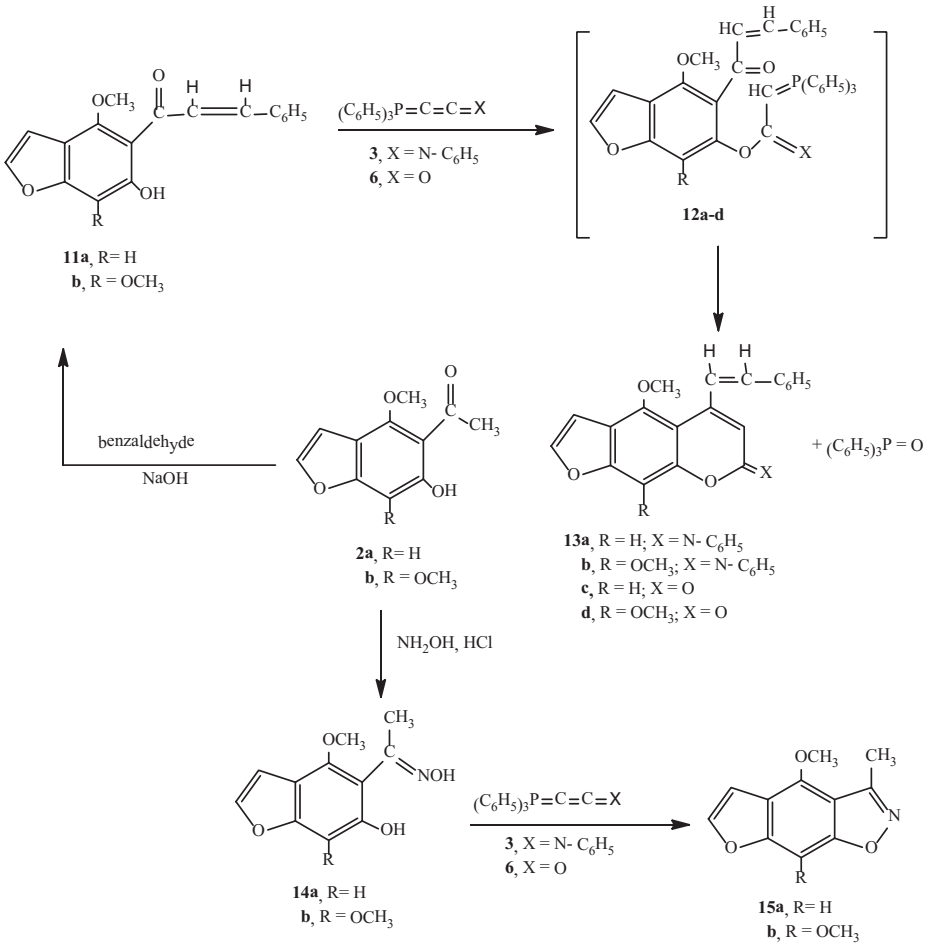

**Scheme 2**

We have studied the reaction of the active phosphacumulenes **3** and **6** with 1-(6-hydroxy-4-methoxybenzofuran-5-yl)-3-phenylprop-2-en-1-one (**11a**) and 1-(6-hydroxy-4,7-dimethoxybenzofuran-5-yl)-3-phenylprop-2-en-1-one (**11b**) in boiling toluene. The reaction completes within 5 h in case of **3** and within 8 h in case of **6**. The corresponding chromenes **13a–d** were obtained together with TPPO. Formation of compounds **13a–d** can be explained by the addition of the phenolic OH group of **11a**,**b** to the phosphacumulenes **3** and **6** to give first the intermediate phosphonium ylides **12a–d**, which are then cyclized to the chromenes **13a–d** with formation of TPPO. The IR and $^1$H NMR spectra of compounds **13a–d** indicate the absence of the phenolic OH groups, which appear in the $^1$H NMR spectra of the starting materials at $\delta = 12.69$ (**11a**) and at $\delta = 12.70$ (**11b**). Furthermore the $^1$H NMR spectrum of **13a** shows the signals of the two protons of the styryl group as two doublets centered at $\delta = 6.74$ and 7.75 ($J_{HH} = 16.1$ Hz), which exclude a [4+2]-cycloaddition and the formation of a pyran structure.

The reaction of 1-(6-hydroxy-4-methoxy-benzofuran-5-yl)ethanone oxime (**14a**) and 1-(6-hydroxy-4,7-dimethoxy-benzofuran-5-yl)ethanone oxime (**14b**) with the phosphacumulenes **3** and **6** was also investigated. Compounds **14a** and **14b** were prepared from the reaction of benzofuran ethanones **2a**,**b** with hydroxylamine hydrochloride.[16] When compounds **14a**,**b** were allowed to react with the phosphoranes **3** and **6** in THF at room temperature for 5 h, 4-methoxy-3-methyl-furo[2′,3′:4,5]benzo[1,2-*d*]isoxazole (**15a**) and 4,8-dimethoxy-3-methyl-furo[2′,3′:4,5]-benzo[1,2-*d*]isoxazole (**15b**) were obtained, respectively. In this case, cyclization occurred with the formation of the isoxazole ring and no reaction was observed between compounds **14a**,**b** and the phosphorus reagents **3** and **6**. The IR and $^1$H NMR spectra of compounds **15a** and **b** indicated the absence of the phenolic and oxime OH groups. In this sense, the phosphacumulene ylides **3** and **6** act as Lewis bases that facilitate the dehydration process. Moreover, when the oximes **14a**,**b** were refluxed in THF for 5 h, compounds **15a**,**b** were obtained only after addition of the base triethylamine to the reaction mixture (Scheme 3).

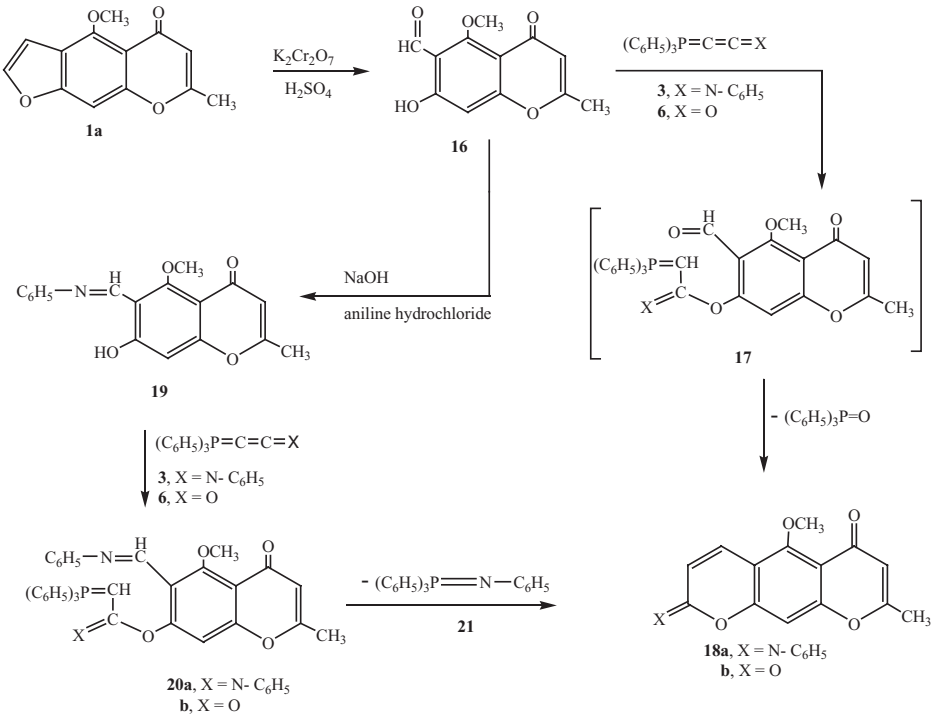
The reaction of 7-hydroxy-5-methyoxy-2-methyl-4-oxo-*4H*-chromene-6-carbald ehyde (**16**) with the phosphacumulenes **3** and **6** was also investigated. Compound **16** was prepared by oxidation of the chromenone **1a** with $K_2Cr_2O_7$ and $H_2SO_4$.[17] Treatment of the chromene carbaldehyde **16** with the phosphoranes **3** or **6** in THF for 10 h in case of **3** and for 15 h in the case of **6** leads to the formation of 5-methoxy-2-methyl-8-phenylimino-*8H*-pyrano[3,2-*g*]chromen-4-one (**18a**) and 5-methoxy-8-methyl-pyrano[3,2-*g*]chromen-2,6-dione (**18b**), respectively. Compounds **18a**,**b** are formed through intramolecular cyclization of the intermediates **17**. The chromenone **18a** shows in the mass spectrum m/z at 335 [M+2H]. In the $^1$H NMR spectrum, no signals corresponding to OH and CHO protons are observed, which appear, however, in the $^1$H NMR spectrum of **16** (Scheme 4).

The reaction of 7-hydroxy-5-methoxy-2-methyl-6-[(phenylimino)methyl]-*4H*-chro men-4-one (**19**) with the phosphacumulene **3** proceeds in THF at room temperature to give the chromenone **18a** together with *N*-phenyliminotriphenylphosphorane (**21**). However when chromenone **19** was allowed to react with phosphacumulene **6** in THF at room temperature for 12 h, the ester (**20b**) was exclusively obtained. When compound **20b** was heated in toluene, cyclization occurs with formation of the corresponding 5-methoxy-8-methyl-pyrano[3,2-*g*]chromene-2,6-dione (**18b**) and the phosphinimine **21**. It is evident that formation of compounds **18a,b** involves the intermediates **20a,b**, which spontaneously lactonize only in case of **20a**. In the mass spectrum of **20b**, the molecular ion peak was found at m/z = 611 ($M^+$, 87%). The $^{31}$P NMR spectrum of **20b** displays a signal at $\delta =$ 22.5 ppm (Scheme 4).

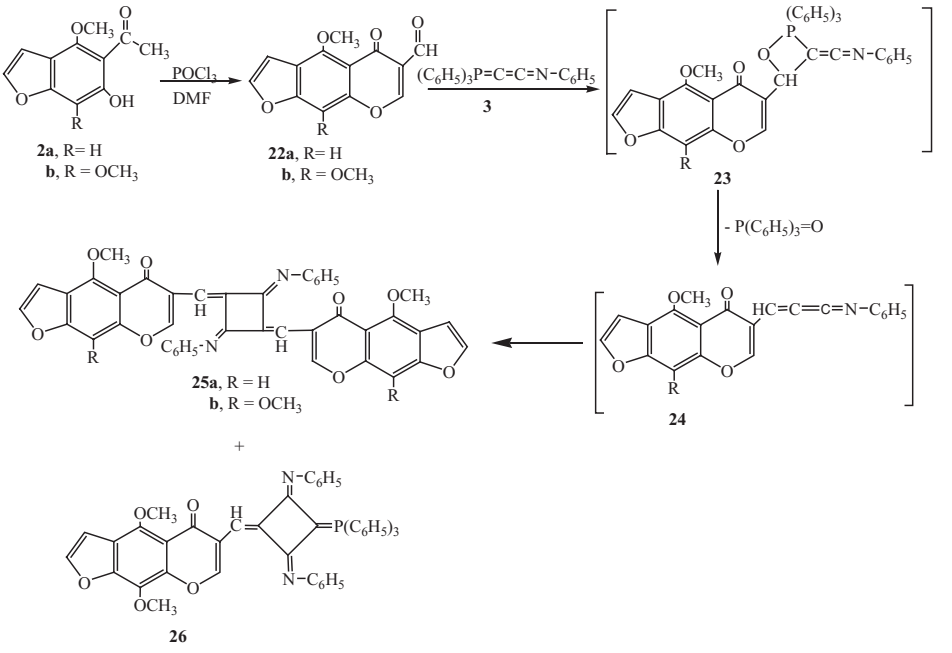



**Scheme 3**

We now report a study on the reaction of the phosphacumulenes **3** and **6** with 4-methoxy-5-oxo-*5H*-furo[3,2-*g*]chromene-6-carbaldehyde (**22a**) and 4,9-dimethoxy-5-oxo-*5H*-furo[3,2-*g*]chromene-6-carbaldehyde (**22b**). Compounds **2a**,**b** are used for the synthesis of the carbaldehydes **22a**,**b** directly via *Vielsmeier–Haack* reaction.[18,19] When the reaction of the chromene carbaldehyde **22a** with the phosphorane **3** was performed in boiling toluene, the corresponding chromen-5-one (**25a**) was obtained. Furthermore reaction of compound **22b** with **3** under the same experimental conditions afforded chromen-5-one (**25b**) and chromen-2-one (**26**). This reaction proceeds via a [2+2]-cycloaddition of the carbonyl group in **22a**,**b** to the ylidic C–P bond of the phosphorane **3** to give the oxaphosphetane **23**.[20–22] Elimenation of TPPO from **23** leads to the formation of the unstable ketene **24**, which dimerizes to give **25a,b**. However in case of the reaction of the chromene carbaldehyde **22b** with the phosphorane **3**, the dimer **25b** was isolated together with the cyclobutylidene chromenone **26**, which is formed by the addition of **3** to the ketene **24** (Scheme 5). The mass spectrum of compound **25a** shows a peak at m/z = 343 ($M^+$, 80%), which corresponds to the molecular ion peak of the monomer. This behavior is frequently observed in the mass



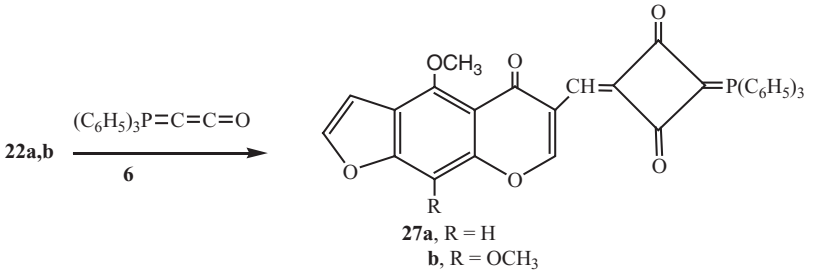

**Scheme 4**




**Scheme 5**

spectra of a variety of dimeric products.[23] The $^{31}P$ NMR spectrum of compound **26** shows a signal at $\delta = 20.7$ ppm, which fits well to a four-membered phosphorane ring structure.[24]

The reactions of the carbaldehydes **22a**,**b** with the phosphacumulene **6** were performed in boiling toluene and yield compounds (**27a**,**b**), respectively. No dimerization product was observed (Scheme 6). The $^{31}P$ NMR signals of compounds **27a** and **27b** are found at 21.72 and 21.66 ppm, respectively.




**Scheme 6**

## CONCLUSION

The fruitful organic chemistry of the phosphacumulene ylides **3** and **6** originates from the unique combination of ylidic and ketene properties resulting in a dipolar electronic structure. The first attack is always that of an electrophile to the ylidic carbanionic carbon atom. The intermediate thus formed can further react in different ways. The outcome and progress of these reactions, which also comprise a selective intramolecular *Wittig* olefination as the actual ring closure step, lead to the formation of a great variety of carbocyclic and heterocyclic organic compounds. Moreover, the difference in the nucleophilic character and reactivity of the phosphacumulene ylides (**3** < **6**) becomes evident in this study.[25] Reagent **3** reacts more smoothly than reagent **6**. These results show new applications of phosphacumulene ylides in the synthesis of some pharmaceutically interesting naturally occurring furo- and pyrano-chromenones.

## EXPERIMENTAL

Melting points (mp) were measured with a Gallenkamp electrothermal digital melting points apparatus. IR spectra were measured as *KBr* pellets with a PerkinElmer Infrared spectrophotometer Model 157. $^{1}H$, $^{13}C$, and $^{31}P$ NMR spectra were recorded in $CDCl_3$ or $d^6$-DMSO with a Varian Spectrometer at 500.1, 125.8, and 202.4 MHz, respectively, using tetramethylsilane (TMS) as internal and 85% H3PO4 as external reference. The mass spectra were recorded at 70 eV with a Kratos MS equipment or a Varian MAT311A Spectrometer. Elemental analyses were performed using the Elementar vario El-Germany Instrument. The experimental values agreed well with the calculated ones.

### Reaction of 1-(6-Hydroxy-4-methoxybenzofuran-5-yl)ethanone (2a) with (*N*-phenyliminovinylidene)triphenylphosphorane (3)

A mixture of (*N*-phenyliminovinylidene)triphenylphosphorane (**3**) (0.37 g, 0.01 mol) and 1-(6-hydroxy-4-methoxybenzofuran-5-yl) ethanone (**2a**) (0.20 g, 0.01 mol) in THF (40

mL) was magnetically stirred at room temperature for 8 h. During which the color of the mixture changed from yellow to brown. The solvent was removed under reduced pressure and the residue was chromatographed on silica gel using petroleum ether (60–80 °C): ethyl acetate (70: 30) as eluent to give compound **5a** as yellow crystals; yield 65%; mp 135 °C. $^1$H NMR (500.1 MHz, $CDCl_3$): $\delta = 2.55$ (d, $J_{HH} = 2.5$ Hz, 3H, $CH_3$), 4.09 (s, 3H, $OCH_3$), 6.09 (q, $J_{HH} = 2.5$ Hz, 1H, 6-H), 6.98 (d, $J_{HH} = 2.30$ Hz, 1H, 3-H of furan ring), 7.01–7.35 (m, 5H, arom-H), 7.14 (s, 1H, 9-H), 7.57 (d, $J_{HH} = 2.30$ Hz, 1H, 2-H of furan ring). $^{13}$C NMR (125.8 MHz, $CDCl_3$): $\delta = 24.3$ ($CH_3$), 61.0 ($OCH_3$), 90.7 (C-9), 106.0 (C-3), 110.2 (C-6), 145.6 (C-5), 146.3 (C-2), 152.2 (C-4), 158.3 (C = N). MS: m/z (%) = 305 ($M^+$, 35.5), 202 ($M^+ - (-C=N-C_6H_5)$, 28.5). Anal. Calcd. for $C_{19}H_{15}O_3N$ (305.33): C, 74.74; H, 4.95; N, 4.59. Found: C, 74.52; H, 4.59; N, 4.25%.

When the reaction was repeated using **2a** (0.20 g, 0.01 mol) and **3** (0.75 g, 0.02 mol), the same product **5a** was isolated.



### Reaction of 1-(6-Hydroxy-4,7-dimethoxybenzofuran-5-yl)ethanone (2b) with (*N*-phenyliminovinylidene)triphenylphosphorane (3)

A solution of (*N*-phenyliminovinylidene)triphenylphosphorane (**3**) (0.37 g, 0.01 mol) in THF (20 mL) was added dropwise with stirring to a solution of 1-(6-Hydroxy-4,7-dimethoxy-benzofuran-5-yl)ethanone (**2b**) (0.25 g, 0.01 mol) in THF (20 mL). The reaction mixture was kept at room temperature for 10 h. The progress of the reaction was followed by thin layer chromatography (TLC). THF was removed under reduced pressure, and the residue was subjected to silica gel column chromatography using petroleum ether (60–80 °C): ethyl acetate (80: 20) as eluent to give the two compounds **5b** and **8b**.

**Compound 5b**: Yellow crystals; yield 65%; mp 128 °C (sharp). $^1$H NMR (500.1 MHz, $CDCl_3$): $\delta = 2.56$ (d, $J_{HH} = 2.50$ Hz, 3H, $CH_3$), 3.81 (s, 3H, $OCH_3$), 4.01 (s, 3H, $OCH_3$), 6.28 (q, $J_{HH} = 2.50$ Hz, 1H, 6-H), 6.89 (d, $J_{HH} = 2.30$ Hz, 1H, 3-H of furan ring), 6.95–7.35 (m, 5H, arom-H), 7.57 (d, $J_{HH} = 2.30$ Hz, 1H, 2-H of furan ring). $^{13}$C NMR (125.8 MHz, $CDCl_3$): $\delta = 23.6$ ($CH_3$), 60.3 ($OCH_3$), 61.7 ($OCH_3$), 105.0 (C-3), 110.2 (C-6), 135.2 (C-9), 143.8 (C-5), 145.7 (C-2), 150.1 (C-4), 156.0 (C=N). MS: m/z (%) = 335 ($M^+$, 27.60), 232 ($M^+ - (-C=N-C_6H_5)$, 5.20). Anal. Calcd. for $C_{20}H_{17}O_4N$ (335.35): C, 71.63; H, 5.11; N, 4.18. Found: C, 71.67; H, 5.12; N, 4.34%.

**Compound 8b**: Yellow crystals; yield 25%; mp 216 °C. IR ($\nu$, $cm^{-1}$): 1610 and 1591 (C=C), 1705 (lactone carbonyl group). $^1$H NMR (500.1 MHz, $CDCl_3$): $\delta = 2.64$ (d, $J_{HH} = 2.5$ Hz, 3H, $CH_3$), 4.07 (s, 3H, $OCH_3$), 4.17 (s, 3H, $OCH_3$), 6.13 (q, $J_{HH} = 2.5$ Hz, 1H, 6-H), 6.96 (d, $J_{HH} = 2.3$ Hz, 1H, 3-H of furan ring), 7.63 (d, $J_{HH} = 2.3$ Hz, 1H, 2-H of furan ring). $^{13}$C NMR (125.8 MHz, $CDCl_3$): $\delta = 24.0$ ($CH_3$), 61.5 ($OCH_3$), 61.7 ($OCH_3$), 105.0 (C-3), 113.9 (C-6), 133.5 (C-9), 146.0 (C-2), 149.0 (C-4), 151.2 (C-5), 160.2 (C=O, lactone). MS: m/z (%) = 260 ($M^+$, 40.0), 232 ($M^+ - (C=O)$, 25.0). Anal. Calcd. for $C_{14}H_{12}O_5$ (260.24): C, 64.61; H, 4.65. Found: C, 64.37; H, 4.39%.

Compound **5b** was boiled in toluene for 3 h; the toluene was removed under reduced pressure and the residue was subjected to silica gel column chromatography using petroleum ether (60–80 °C): chloroform (70: 30) as an eluent to give compound **8b** and traces of compound **5b**.

### Reaction of 1-(6-Hydroxy-4-methoxybenzofuran-5-yl)ethanone (2a) or 1-(6-Hydroxy-4,7-di-methoxybenzofuran-5-yl)ethanone (2b) with (2-Oxovinylidene)triphenylphosphorane (6)

To a solution of 1-(6-hydroxy-4-methoxybenzofuran-5-yl) ethanone (**2a**) (0.20 g, 0.01 mol) or 1-(6-hydroxy-4,7-dimethoxybenzofuran-5-yl) ethanone (**2b**) (0.25 g, 0.01 mol) in dry THF (20 mL) was added a solution of (2-oxovinylidene)triphenylphosphorane (**6**) (0.30 g, 0.01 mol) in dry THF (20 mL). The reaction mixture was stirred at room temperature during 8–12 h. THF was removed under reduced pressure. The residue was subjected to silica gel column chromatography using petroleum ether (60–80 °C): acetone (70: 30) as eluent to give **7a** or **7b**, respectively.

**Compound 7a**: Pale yellow crystals; yield 70%; mp 260 °C. $^1$H NMR (500.1 MHz, $CDCl_3$): $\delta = 2.56$ (s, 3H, $CH_3$), 4.06 (s, 3H, $OCH_3$), 5.23 (d, $^2J_{PH} = 15.0$ Hz, 1H, H–C=P), 6.86 (d, $J_{HH} = 2.3$ Hz, 1H, 3-H of furan ring), 7.26 (s, 1H, 7-H), 7.58 (d, $J_{HH} = 2.3$ Hz, 1H, 2-H of furan ring), 7.50–7.74 (m, 15H, arom-H). $^{13}$C NMR (125.8 MHz, $CDCl_3$): $\delta =$ 32.6 ($CH_3$), 60.8 ($OCH_3$), 95.9 (C-7), 105.3 (C-3), 116.3 (C-5), 145.8 (C-2), 151.4 (C-4), 153.7 (C-6), 155.4 (–C=P), 161.0 (–O–C=O), 202.0 ($CH_3$–C=O). $^{31}$P NMR (202.4 MHz, $CDCl_3$): $\delta = 17.4$. MS: m/z (%) = 508 ($M^+$, 25.3), 262 ($P(C_6H_5)_3$, 100), 246 ($M^+ - P(C_6H_5)_3$, 5.90). Anal. Calcd. for $C_{31}H_{25}O_5P$ (508.5): C, 73.22; H, 4.96; P, 6.09. Found: C, 73.12; H, 4.51; P, 6.43%.

**Compound 7b**: Brown crystals; yield 35%; mp 200 °C. $^1$H NMR (500.1 MHz, $CDCl_3$): $\delta = 2.22$ (s, 3H, $CH_3$), 3.90 (s, 3H, $OCH_3$), 4.10 (s, 3H, $OCH_3$), 5.26 (d, $^2J_{PH} =$ 15.0 Hz, 1H, H–C=P), 6.80 (d, $J_{HH} = 2.3$ Hz, 1H, 3-H of furan ring), 7.59 (d, $J_{HH} = 2.3$ Hz, 1H, 2-H of furan ring), 7.26–7.74 (m, 15H, arom-H). $^{13}$C NMR (125.8 MHz, $CDCl_3$): $\delta = 32.8$ ($CH_3$), 60.8 ($OCH_3$), 61.3 ($OCH_3$), 106.3 (C-3), 113.0 (C-5), 135.5 (C-7), 145.9 (C-2), 150.2 (C-4), 153.0 (C-6), 154.4 (–C=P), 161.2 (–O–C=O), 201.0 ($CH_3$–C=O). $^{31}$P NMR (202.4 MHz, $CDCl_3$): $\delta = 17.8$. MS: m/z (%) = 540 (M+2, 22.6), 262 ($P(C_6H_5)_3$, 90.0), 278 (M+2 − $P(C_6H_5)_3$, 24.3). Anal. Calcd. for $C_{32}H_{27}O_6P$ (538.53): C, 71.37; H, 5.05; P, 5.75. Found: C, 71.21; H, 4.99; P, 5.52%.

When compounds **7a** and **7b** were boiled in toluene, they were converted into compounds **8a** and **8b**, respectively, and TPPO.

**Compound 8a**: Yellow crystals; yield 55%; mp 172 °C, IR ($\nu$, $cm^{-1}$): 1618 and 1591 (C=C), 1731 (lactone carbonyl group). $^1$H NMR (500.1 MHz, $CDCl_3$): $\delta = 2.61$ (d, $J_{HH} =$ 2.5 Hz, 3H, $CH_3$), 4.14 (s, 3H, $OCH_3$), 6.06 (q, $J_{HH} = 2.5$ Hz, 1H, 6-H), 6.95 (s, 1H, 9-H), 6.98 (d, $J_{HH} = 2.3$ Hz, 1H, 3-H of furan ring), 7.56 (d, $J_{HH} = 2.3$ Hz, 1H, 2-H of furan ring). $^{13}$C NMR (125.8 MHz, $CDCl_3$): $\delta = 24.4$ ($CH_3$), 60.8 ($OCH_3$), 95.1 (C-9), 105.2 (C-3), 113.5 (C-6), 144.9 (C-2), 151.9 (C-4), 152.9 (C-5), 160.9 (C=O). MS: m/z (%) = 230 ($M^+$, 100), 202 ($M^+ -$ (C=O), 28.0). Anal. Calcd. for $C_{13}H_{10}O_4$ (230.22): C, 67.82; H, 4.38. Found: C, 67.51; H, 4.21%.

### Reaction of Phosphoranes 3 and 6 with Compounds 11a,b: General Procedure

A solution of **11a** or **11b** (0.01 mol) in toluene (20 mL) was added under reflux and stirring to a solution of phosphacumulenes **3** or **6** (0.02 mol) in toluene (20 mL). The reaction mixture was left for 5 h when **3** was used and for 8 h in the case of **6**. The progress of the reaction was monitored by TLC. Toluene was distilled off under reduced pressure,

and the remaining material was chromatographed on silica gel to give TPPO (mp and mixed mp 151 °C) and compounds **13a–d**.

### *N*-(4-Methoxy-5-styryl-7*H*-furo[3,2-*g*]chromen-7-ylidene)benzenamine (13a)

Orange crystals; mp 168 °C; yield 87%; chromatography on silica gel with petroleum ether/chloroform as eluent (60: 40). $^1$H NMR (500.1 MHz, $CDCl_3$): $\delta = 4.03$ (s, 3H, $OCH_3$), 6.32 (s, 1H, 6-H), 6.88 (d, $J_{HH} = 2.3$ Hz, 1H, 3-H of furan ring), 6.89 (s, 1H, 9-H), 7.53 (d, $J_{HH} = 2.3$ Hz, 1H, 2-H of furan ring), 6.74 (d, $J_{HH} = 16.1$ Hz, 1H, CH=CH), 7.75 (d, $J_{HH} = 16.1$ Hz, 1H, CH=CH), 7.08–7.48 (m, 10H, arom-H). $^{13}$C NMR (125.8 MHz, $CDCl_3$): $\delta = 61.6$ ($OCH_3$), 95.6 (C-9), 106.6 (C-3), 108.7 (C-6), 132.0 (CH=CH), 127.0 (CH=CH), 146.3 (C-2), 150.2 (C-4), 152.1 (C-5), 156.0 (C=N). MS: m/z (%) = 393 ($M^+$, 32.9), 290 ($M^+ -$ (–CH=CH–$C_6H_5$), 100), 199 ($M^+ -$ (–CH=CH–$C_6H_5$) and (–N–$C_6H_5$), 2.56). Anal. Calcd. for $C_{26}H_{19}O_3N$ (393.43): C, 79.37; H, 4.87; N, 3.56. Found: C, 79.20; H, 4.68; N, 3.45%.

### *N*-(4,9-Dimethoxy-5-styryl-7*H*-furo[3,2-*g*]chromen-7-ylidene)-benzenamine (13b)

Yellow crystals; yield 68%; mp 153–155 °C; chromatography on silica gel with petroleum ether/acetone as eluent (60: 40) and recrystallized from benzene. $^1$H NMR (500.1 MHz, $CDCl_3$): $\delta = 3.86$ (s, 3H, $OCH_3$), 4.02 (s, 3H, $OCH_3$), 6.32 (s, 1H, 6-H), 6.87 (d, $J_{HH} = 2.3$ Hz, 1H, 3-H of furan ring), 6.76 (d, $J_{HH} = 16.1$ Hz, 1H, CH=CH), 7.83 (d, $J_{HH} = 16.1$ Hz, 1H, CH=CH), 7.00–7.57 (m, 10H, arom-H), 7.76 (d, $J_{HH} = 2.3$ Hz, 1H, 2-H of furan ring). $^{13}$C NMR (125.8 MHz, $CDCl_3$): $\delta = 61.6$ ($OCH_3$), 62.1 ($OCH_3$), 106.9 (C-3), 109.7 (C-6), 132.2 (CH=CH), 127.0 (CH=CH), 137.0 (C-9), 146.2 (C-2), 149.7 (C-4), 152.4 (C-5), 155.0 (C=N). MS: m/z (%) = 424 ($M^+$, 35.6), 321 ($M^+ -$ (–CH=CH–$C_6H_5$), 88.0), 230 ($M^+ -$ (–CH=CH–$C_6H_5$) and (–N–$C_6H_5$), 14.6). Anal. Calcd. for $C_{27}H_{21}O_4N$ (423.46): C, 76.58; H, 5.00; N, 3.31. Found: C, 76.21; H, 4.87; N, 3.27%.

### 4-Methoxy-5-styryl-7*H*-furo[3,2-*g*]chromen-7-one (13c)

Yellow crystals; yield 75%; mp 175 °C (sharp); chromatography on silica gel with *n*-hexane/ethyl acetate (70: 30) as eluent. IR ($\nu$, $cm^{-1}$): 1710 (lactone carbonyl group), 1625 (C=C). $^1$H NMR (500.1 MHz, $CDCl_3$): $\delta = 4.02$ (s, 3H, $OCH_3$), 6.39 (s, 1H, 6-H), 6.88 (d, $J_{HH} = 2.3$ Hz, 1H, 3-H of furan ring), 6.94 (s, 1H, 9-H), 7.61 (d, $J_{HH} = 2.3$ Hz, 1H, 2-H of furan ring), 7.03 (d, $J_{HH} = 16.1$ Hz, 1H, CH=CH), 7.87 (d, $J_{HH} = 16.1$ Hz, 1H, CH=CH), 6.98–7.32 (m, 5H, arom-H). $^{13}$C NMR (125.8 MHz, $CDCl_3$): $\delta = 62.0$ ($OCH_3$), 97.2 (C-9), 104.9 (C-3), 111.2 (C-6), 131.1 (CH=CH), 125.9 (CH=CH), 145.7 (C-2), 148.0 (C-4), 150.8 (C-5), 160.3 (C=O). MS: m/z (%) = 318 ($M^+$, 100), 215 ($M^+ -$ (–CH=CH–$C_6H_5$), 19.2), 187 ($M^+ -$ (–CH=CH–$C_6H_5$) and (C=O), 11.4). Anal. Calcd. for $C_{20}H_{14}O_4$ (318.32): C, 75.46; H, 4.43. Found: C, 75.09; H, 4.03%.

### 4,9-Dimethoxy-5-styryl-7*H*-furo[3,2-*g*]chromen-7-one (13d)

Orange crystals; yield 65%; mp 186–187 °C; chromatography on silica gel with petroleum ether/acetone (80: 20) as eluent. IR ($\nu$, $cm^{-1}$): 1709 (lactone carbonyl group), 1621 (C=C). $^1$H NMR (500.1 MHz, $CDCl_3$): $\delta = 3.91$ (s, 3H, $OCH_3$), 4.18 (s, 3H, $OCH_3$),

6.41 (s, 1H, 6-H), 6.93 (d, $J_{HH} = 2.3$ Hz, 1H, 3-H of furan ring), 7.57 (d, $J_{HH} = 2.3$ Hz, 1H, 2-H of furan ring), 7.03 (d, $J_{HH} = 16.1$ Hz, 1H, CH=CH), 7.88 (d, $J_{HH} = 16.1$ Hz, 1H, CH=CH), 7.00–7.23 (m, 5H, arom-H). $^{13}$C NMR (125.8 MHz, $CDCl_3$): $\delta = 61.6$ ($OCH_3$), 62.1 ($OCH_3$), 104.7 (C-3), 110.2 (C-6), 132.9 (CH=CH), 126.8 (CH=CH), 136.8 (C-9), 145.4 (C-2), 149.3 (C-4), 155.6 (C-5), 160.4 (C=O). MS; m/z (%) = 348 ($M^+$, 68.8), 245 ($M^+ -$ (–CH=CH–$C_6H_5$), 18.0), 217 ($M^+ -$ (–CH=CH–$C_6H_5$) and (C=O), 12.2). Anal. Calcd. for $C_{21}H_{16}O_5$ (348.35): C, 72.41; H, 4.63. Found: C, 72.67; H, 4.34%.

### Reaction of Oxime 14a with Phosphacumulenes 3 and 6

Phosphacumulene **3** (0.37 g, 0.01 mol) or **6** (0.30 g, 0.01 mol) was added to oxime **14a** (0.22 g, 0.01 mol) in THF (30 mL) under stirring at room temperature for 5 h. THF was distilled off under reduced pressure, and the remaining residue was chromatographed on silica gel using petroleum ether (60–80 °C)/ethyl acetate as eluent (80: 20) to give isoxazole **15a** as white crystals, yield 80%, mp 115 °C (sharp). $^1$H NMR (500.1 MHz, $CDCl_3$): $\delta = 2.66$ (s, 3H, $CH_3$), 4.09 (s, 3H, $OCH_3$), 7.27 (s, 1H, 8-H), 6.99 (d, $J_{HH} = 2.3$ Hz, 1H, 3-H of furan ring), 7.57 (d, $J_{HH} = 2.3$ Hz, 1H, 2-H of furan ring). $^{13}$C NMR (125.8 MHz, $CDCl_3$): $\delta = 18.2$ ($CH_3$), 61.1 ($OCH_3$), 93.5 (C-8), 105.9 (C-3), 147.0 (C-2), 149.3 (C-4), 155.1 (C-5). MS: m/z (%) = 203 ($M^+$, 100), 189 ($M^+ -$ ($CH_2$), 46.1). Anal. Calcd. for $C_{11}H_9NO_3$ (203.19): C, 65.02; H, 4.46; N, 6.89. Found: C, 64.92; H, 4.35; N, 6.52%.

### Reaction of Oxime 14b with Phosphacumulenes 3 and 6

A solution of phosphacumulene **3** (0.37 g, 0.01 mol) or **6** (0.3 g, 0.01 mol) in THF (20 mL) was added to a solution of oxime **14b** (0.26 g, 0.01 mol) in THF (20 mL) with stirring at room temperature for 5 h. THF was distilled off under reduced pressure, and the remaining residue was chromatographed on silica gel using petroleum ether (60–80 °C)/ethyl acetate (60: 40) as eluent to give isoxazole **15b** as white crystals, yield 80%, mp 152–154 °C. $^1$H NMR (500.1 MHz, $CDCl_3$), $\delta = 2.65$ (s, 3H, $CH_3$), 4.05 (s, 3H, $OCH_3$), 4.17 (s, 3H, $OCH_3$), 6.99 (d, $J_{HH} = 2.3$ Hz, 1H, 3-H of furan ring), 7.57 (d, $J_{HH} = 2.3$ Hz, 1H, 2-H of furan ring). $^{13}$C NMR (125.8 MHz, $CDCl_3$): $\delta = 18.0$ ($CH_3$), 60.9 ($OCH_3$), 61.3 ($OCH_3$), 105.0 (C-3), 135.7 (C-8), 146.4 (C-2), 151.1 (C-4), 156.6 (C-5). MS: m/z (%) = 233 ($M^+$, 100), 219 ($M^+ -$ ($CH_2$), 49.0). Anal. Calcd. for $C_{12}H_{11}NO_4$ (233.22): C, 61.80; H, 4.75; N, 6.01. Found: C, 61.48; H, 4.86; N, 6.09%.

When a solution of the oximes **14a,b** in THF was refluxed for 5 h with a few drops of triethylamine, compounds **15a,b** were obtained.

### Reaction of 4*H*-chromene-6-carbaldehyde 16 with Phosphacumulenes 3 or 6

A mixture of **16** (0.26 g, 0.01 mol) and phosphacumulenes **3** or **6** (0.01 mol) in dry THF (20 mL) was stirred at room temperature for 10 h in case of **3** and for 15 h in case of **6**, until no more of the starting materials could be detected (TLC). THF was distilled off under reduced pressure and the remaining residue was chromatographed on silica gel using *n*-hexane/acetone (80: 20) as eluent to give **18a** or **18b**, respectively, and TPPO (mp and mixed mp 151 °C).

### 5-Methoxy-2-methyl-8-phenylimino-8*H*-pyrano[3,2-*g*]chromen-4-one (18a)

Yellow crystals; yield 70%; mp 140 °C. IR ($\nu$, $cm^{-1}$): 1663 ($\gamma$-pyrone carbonyl group), 1625 (C=N). $^1H$ NMR (500.1 MHz, $CDCl_3$): $\delta = 2.35$ (d, $J_{HH} = 2.5$ Hz, 3H, $CH_3$), 4.02 (s, 3H, $OCH_3$), 6.08 (q, $J_{HH} = 2.5$ Hz, 1H, 7-H), 6.40 (d, $J_{HH} = 9.7$ Hz, 1H, H of $\alpha$-pyrone ring), 8.08 (d, $J_{HH} = 9.7$ Hz, 1H, H of $\alpha$-pyrone ring), 7.08–7.65 (m, 6H, arom-H, 10-H). $^{13}C$ NMR (125.8 MHz, $CDCl_3$): $\delta = 20.1$ ($CH_3$), 64.3 ($OCH_3$), 101.4 (C-10), 111.7 (C-7), 115.7 (C-3), 138.4 (C-4), 156.8 (C-5), 159.5 (C=N), 165.1 (C-8), 176.5 ($\gamma$-pyrone carbonyl group). MS: m/z (%) = 335 (M+2, 32.8), 258 (M+2 − (–$C_6H_5$), 19.4), 230 (M+2 − (C=N–$C_6H_5$), 26.9). Anal. Calcd. for $C_{20}H_{15}O_4N$ (333.34): C, 72.06; H, 4.54; N, 4.20. Found: C, 72.35; H, 4.29; N, 4.06%.

### 5-Methoxy-8-methyl-pyrano[3,2-*g*]chromene-2,6-dione (18b)

Brown powder; yield 45%, mp 235 °C (sharp). IR ($\nu$, $cm^{-1}$): 1663 ($\gamma$-pyrone carbonyl group) and 1746 (lactone carbonyl group). $^1H$ NMR (500.1 MHz, $CDCl_3$): $\delta = 2.36$ (d, $J_{HH} = 2.5$ Hz, 3H, $CH_3$), 4.03 (s, 3H, $OCH_3$), 6.09 (q, $J_{HH} = 2.5$ Hz, 1H, 7-H), 7.09 (s, 1H, 10-H), 6.40 (d, $J_{HH} = 9.7$ Hz, 1H, H of $\alpha$-pyrone ring), 8.09 (d, $J_{HH} = 9.7$ Hz, 1H, H of $\alpha$-pyrone ring). $^{13}C$ NMR (125.8 MHz, $CDCl_3$): $\delta = 20.1$ ($CH_3$), 64.2 ($OCH_3$), 101.3 (C-10), 111.7 (C-7), 115.7 (C-3), 138.4 (C-4), 156.4 (C-5), 160.0 (lactone carbonyl group), 164.8 (C-8), 176.4 ($\gamma$-pyrone carbonyl group). MS: m/z (%) = 258 ($M^+$, 34.4), 230 ($M^+$ − (C=O), 13.0). Anal. Calcd. for $C_{14}H_{10}O_5$ (258.23): C, 65.12; H, 3.90. Found: C, 65.07; H, 3.79%.

### Reaction of 4*H*-Chromen-4-one 19 with Phosphacumulene 3

A mixture of **19** (0.30 g, 0.01 mol) and phosphacumulene **3** (0.75 g, 0.02 mol) was stirred in 30 mL of dry THF at room temperature for 8 h. THF was distilled under reduced pressure, and the residue was crystallized from benzene to give compound **18a** and the phosphinimine **21**.

### Reaction of 4*H*-Chromen-4-one 19 with Phosphacumulene 6

A mixture of **19** (0.30 g, 0.01 mol) and phosphacumulene **6** (0.6 g, 0.02 mol) was stirred in 30 mL of dry THF at room temperature for 12 h. THF was distilled off under reduced pressure, and the remaining residue was crystallized from cyclohexane to give compound **20b**.

**Compound 20b**: Yellow crystals; yield 75%; mp 110 °C. $^1H$ NMR (500.1 MHz, $CDCl_3$): $\delta = 2.24$ (d, $J_{HH} = 2.5$, 3H, $CH_3$), 3.83 (s, 3H, $OCH_3$), 4.57 ($^2J_{PH} = 15.4$ Hz, 1H, –P=C–H), 6.14 (q, $J_{HH} = 2.5$, 1H, vinyl-H), 7.09 (s, 1H, 8-H), 7.01–7.98 (m, 20H, arom-H), 8.39 (s, 1H, –N=C–H). $^{13}C$ NMR (125.8 MHz, $CDCl_3$): $\delta = 20.7$ ($CH_3$), 61.8 ($OCH_3$), 111.0 (C-3), 150.6 (C-2), 153.5 (C-5), 155.3 (P=C), 157.5 (C-7), 159.8 (N=C), 164.0 (O = C–O), 175.7 (pyrone carbonyl ring). $^{31}P$ NMR (202.4 MHz, $CDCl_3$): $\delta = 22.5$. MS: m/z (%) = 611 ($M^+$, 87.0), 262 ($P(C_6H_5)_3$, 66.1), 349 ($M^+ - P(C_6H_5)_3$, 24.0). Anal. Calcd. for $C_{38}H_{30}O_5NP$ (611.62): C, 74.62; H, 4.94; N, 2.29; P, 5.06. Found: C, 74.22; H, 4.72; N, 2.10; P, 5.00%.

When the compound **20b** was boiled in toluene, it was converted to compound **18b** and the phosphinimine **21**.

### Reaction of Carbaldehyde 22a with Phosphorane 3

A solution of phosphacumulene **3** (0.75 g, 0.02 mol) in 20 mL of toluene was added dropwise with stirring and refluxing to a solution of **22a** (0.24 g, 0.01 mol) in 20 mL of toluene. The reaction mixture was stirred for 5 h. The progress of the reaction was monitored by TLC. Toluene was distilled off under reduced pressure, and the remaining residue was crystallized from cyclohexane to give compound **25a** as yellow crystals, yield 78%, mp 192 °C (sharp). IR ($\nu$, $cm^{-1}$): 1663 ($\gamma$-pyrone carbonyl group) and 1610 (C=C). $^1$H NMR (500.1 MHz, $CDCl_3$): $\delta$ = 4.03 (s, 6H, $OCH_3$), 6.47 (s, 2H, –CH=C), 6.82 (s, 2H, 9-H), 6.70 (d, $J_{HH}$ = 2.3 Hz, 2H, 3-H of furan rings), 7.53 (d, $J_{HH}$ = 2.3 Hz, 2H, 2-H of furan rings), 7.25–7.68 (m, 12H, arom-H, 7-H). $^{13}$C NMR (125.8 MHz, $CDCl_3$): $\delta$ = 62.0 ($OCH_3$), 159.0 (C=N), 177.3 (pyrone carbonyl ring). MS: m/z (%) = 343 ($M^+$ for monomer, 80.0). Anal. Calcd. for $C_{42}H_{26}O_8N_2$ (686.66): C, 73.46; H, 3.82; N, 4.08. Found: C, 73.25; H, 3.50; N, 4.00%.

### Reaction of Carbaldehyde 22b with Phosphorane 3

A mixture of phosphacumulene **3** (0.75 g, 0.02 mol) and **22b** (0.27 g, 0.01 mol) in toluene (30 mL) was refluxed for 8 h. During this time the color of the reaction solution changed from yellow to dark brown. Toluene was distilled off under reduced pressure and the remaining residue was chromatographed on silica gel using petroleum ether (60–80 °C)/ethyl acetate (50: 50) as eluent to give the products **25b** and **26**.

**Compound 25b**: Yellow crystals; yield 30%; mp 215 °C. IR ($\nu$, $cm^{-1}$): 1672 ($\gamma$-pyrone carbonyl group) and 1638 (C=C). $^1$H NMR (500.1 MHz, $CDCl_3$): $\delta$ = 3.65 (s, 6H, $OCH_3$), 3.87 (s, 6H, $OCH_3$), 6.66 (s, 2H, –CH=C), 6.69 (d, $J_{HH}$ = 2.3 Hz, 2H, 3-H of furan rings), 7.57 (d, $J_{HH}$ = 2.3 Hz, 2H, 2-H of furan rings), 6.86–7.49 (m, 12H, arom-H, 7-H). $^{13}$C NMR (125.8 MHz, $CDCl_3$): $\delta$ = 61.2 ($OCH_3$), 62.0 ($OCH_3$), 105.0 (C-3), 119.7 (C=CH), 124.6 (C-9), 144.8 (CH=C), 145.2 (C-2), 145.7 (C-4), 157.9 (C=N), 177.5 (pyrone carbonyl ring). MS: m/z (%) = 373 ($M^+$ for monomer, 45). Anal. Calcd. for $C_{44}H_{30}O_{10}N_2$ (746.72): C, 70.77; H, 4.05; N, 3.75. Found: C, 70.75; H, 4.09; N, 3.53%.

**Compound 26**: Yellow crystals; yield 55%; mp 172 °C. $^1$H NMR (500.1 MHz, $CDCl_3$): $\delta$ = 3.88 (s, 3H, $OCH_3$), 4.02 (s, 3H, $OCH_3$), 6.66 (d, $J_{HH}$ = 2.3 Hz, 1H, 3-H of furan ring), 7.23 (s, 1H, HC-7), 7.44 (s, 1H, CH=C), 7.45 (d, $J_{HH}$ = 2.3 Hz, 1H, 2-H of furan ring), 7.50–7.98 (m, 25H, arom-H). $^{13}$C NMR (125.8 MHz, $CDCl_3$): $\delta$ = 61.0 ($OCH_3$), 61.5 ($OCH_3$), 105.0 (C-3), 143.0 (C-4), 145.0 (C-2), 150.8 (C-7), 153.8 (d, $^1J_{PC}$ = 93.0 Hz, C=P), 180.8 (HC=C), 151.9 (HC=C), 165.2 (C=N), 177.2 (pyrone carbonyl ring). $^{31}$P NMR (202.4 MHz, $CDCl_3$): $\delta$ = 20.7. Anal. Calcd. for $C_{48}H_{35}O_5N_2P$ (750.78): C, 76.79; H, 4.70; N, 3.73; P, 4.13. Found: C, 76.61; H, 4.63; N, 3.69; P, 4.22%.

### Reaction of (2-Oxovinylidene)triphenylphosphorane (6) with Compounds 22a,b

To a solution of (2-oxovinylidene)triphenylphosphorane (**6**) (0.6 g, 0.02 mol) in 20 mL of toluene was added a solution of **22a** or **22b** (0.01 mol) in 20 mL of toluene. The reaction mixture was refluxed for 12 h. The solvent was removed under reduced pressure,

and the residue was chromatographed on silica gel using *n*-hexane/acetone (70: 30) as eluent to give **27a** or **27b**, respectively.

**Compound 27a**: Yellow crystals; yield 67%; mp 143–145 °C. IR ($\nu$, $cm^{-1}$): 1663 ($\gamma$-pyrone carbonyl group), 1701 (cyclobutane carbonyl groups). $^1$H NMR (500.1 MHz, $CDCl_3$): $\delta$ = 3.89 (s, 3H, $OCH_3$), 6.72 (s, 1H, 9-H), 6.75 (d, $J_{HH}$ = 2.3 Hz, 1H, 3-H of furan ring), 7.34 (s, 1H, 7-H), 7.44 (d, $J_{HH}$ = 2.3 Hz, 1H, 2-H of furan ring), 7.45–7.62 (m, 15H, arom-H), 7.67 (s, 1H, CH=C). $^{13}$C NMR (125.8 MHz, $CDCl_3$): $\delta$ = 60.5 ($OCH_3$), 94.2 (C-9), 105.3 (C-3), 142.6 (C-4), 145.6 (C-2), 147.3 (C-7), 152.0 (HC=C), 156.1 (d, $^1J_{PC}$ = 92.4 Hz, C=P), 176.0 (pyrone carbonyl ring), 179.3 (CH=C), 189.98 (C=O cyclobutylidene), 190.02 (C=O, cyclobutylidene). $^{31}$P NMR (202.4 MHz, $CDCl_3$): $\delta$ = 21.7. Anal. Calcd. for $C_{35}H_{23}O_6P$ (570.53): C, 73.68; H, 4.06; P, 5.43. Found: C, 73.60; H, 3.99; P, 5.39%.

**Compound 27b**: Yellow crystals; yield 70%; mp 205 °C (sharp). IR ($\nu$, $cm^{-1}$): 1652 ($\gamma$-pyrone carbonyl group), 1710 (carbonyl group). $^1$H NMR (500.1 MHz, $CDCl_3$): $\delta$ = 3.81 (s, 3H, $OCH_3$), 4.01 (s, 3H, $OCH_3$), 6.76 (d, $J_{HH}$ = 2.3 Hz, 1H, 3-H of furan ring), 7.33 (s, 1H, 7-H), 7.38 (d, $J_{HH}$ = 2.3 Hz, 1H, 2-H of furan ring), 7.55–7.63 (m, 15H, arom-H), 7.64 (s, 1H, CH=C). $^{13}$C NMR (125.8 MHz, $CDCl_3$): $\delta$ = 61.0 ($OCH_3$), 61.5 ($OCH_3$), 105.9 (C-3), 124.4 (C-9), 146.0 (C-2), 147.2 (C-4), 148.7 (C-7), 151.0 (HC=C), 154.7 (d, $^1J_{PC}$ = 97.3 Hz, C=P), 177.2 (pyrone carbonyl ring), 180.5 (HC=C), 189.8 (C=O, cyclobutylidene), 191.4 (C=O, cyclobutylidene). $^{31}$P NMR (202.4 MHz, $CDCl_3$): $\delta$ = 21.7. Anal. Calcd. for $C_{36}H_{25}O_7P$ (600): C, 72.00; H, 4.20; P, 5.16. Found: C, 72.01; H, 4.30; P, 5.28%.

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