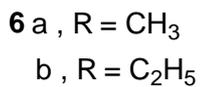
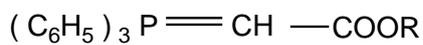
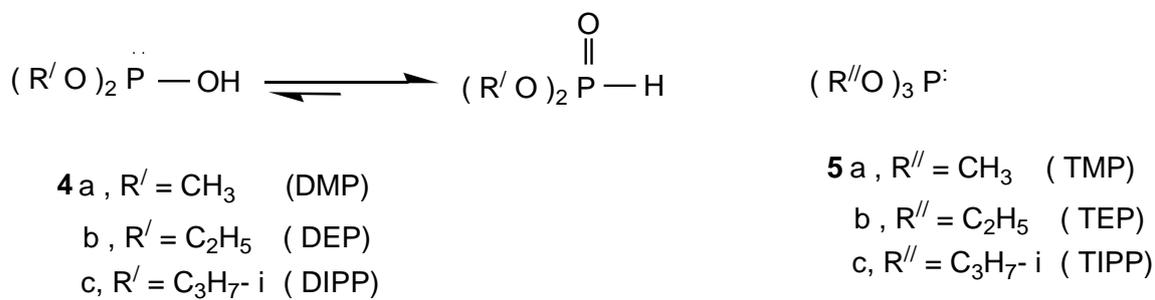
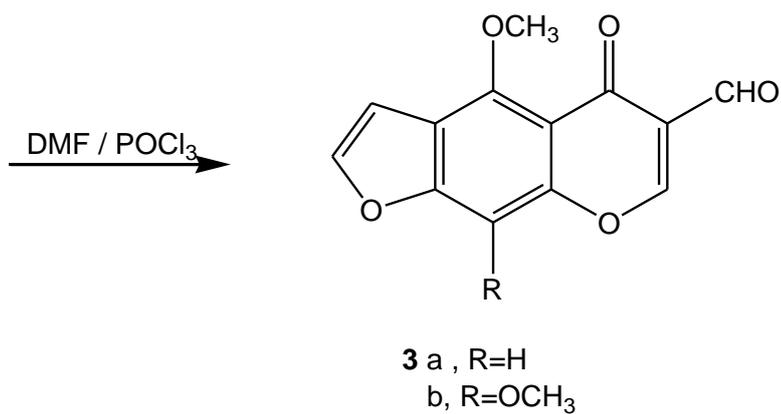
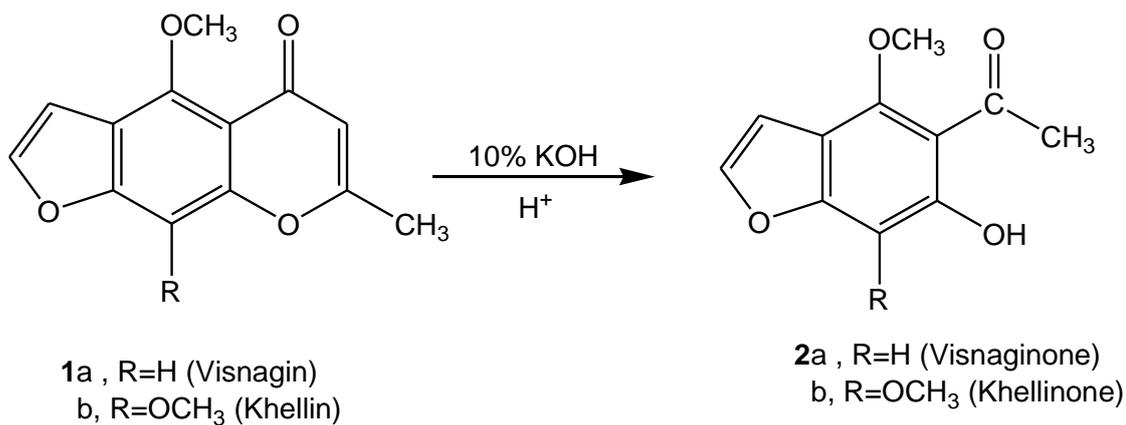


Part I

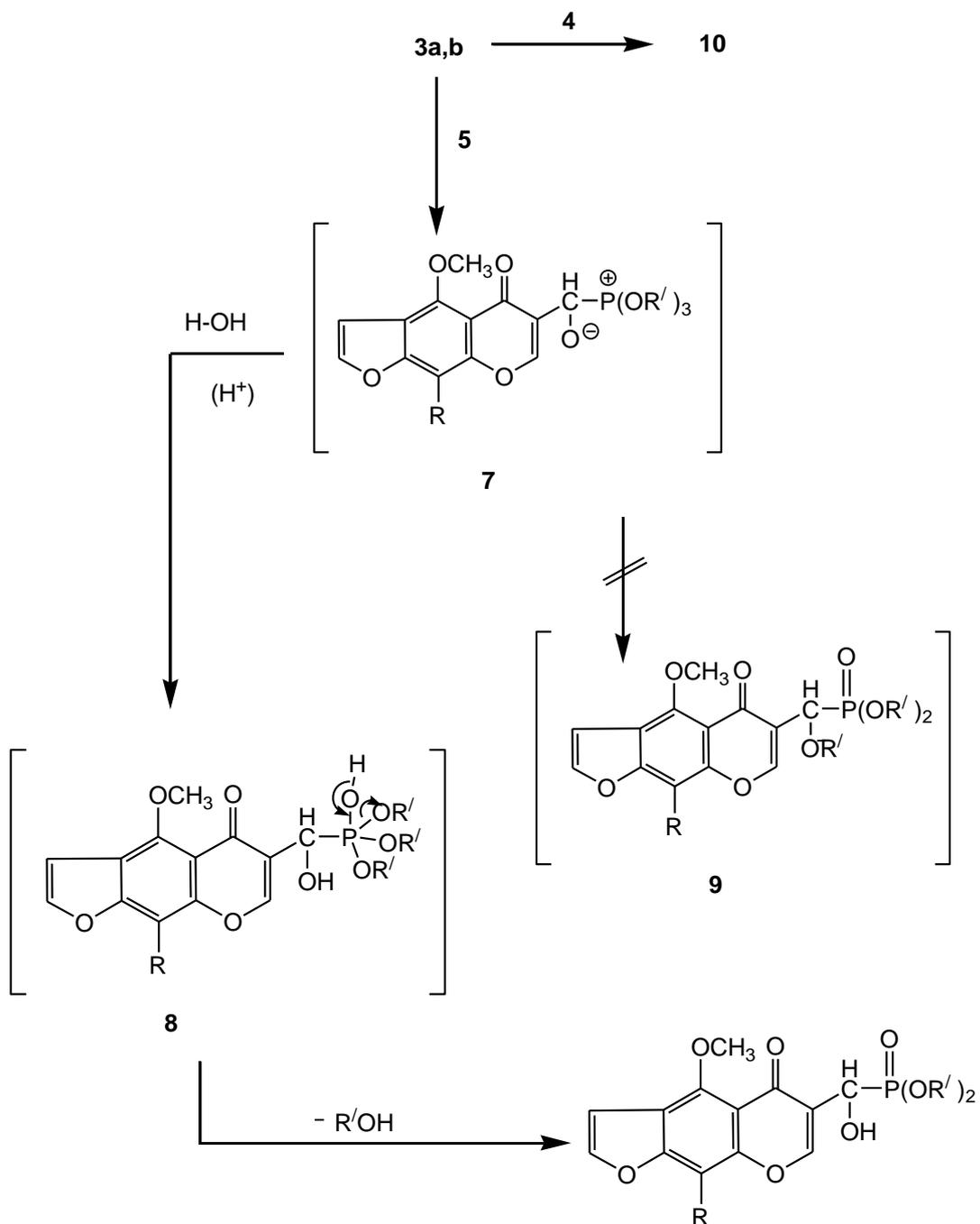
Reactions of Furobenzopyran-6-carboxaldehydes with Alkyl Phosphites and Ylidenetriphenylphosphoranes (Wittig Reagents)

The starting materials, namely 4-methoxy-5-oxo-5H-furo[3,2-g]benzopyran-6-carboxaldehyde **3a** and 4,9-dimethoxy-5-oxo-5H-furo[3,2-g]benzopyran-6-carboxaldehyde **3b** are prepared *via* alkali hydrolysis of the naturally occurring visnagin **1a** and khellin **1b**, respectively followed by reacting the produced visnaginone **2a** and khellinone **2b** with N,N-dimethylformamide (DMF) in the presence of phosphoryl chloride under conditions of Vielsmeier-Haak reaction (**Scheme 1**).



Scheme 1

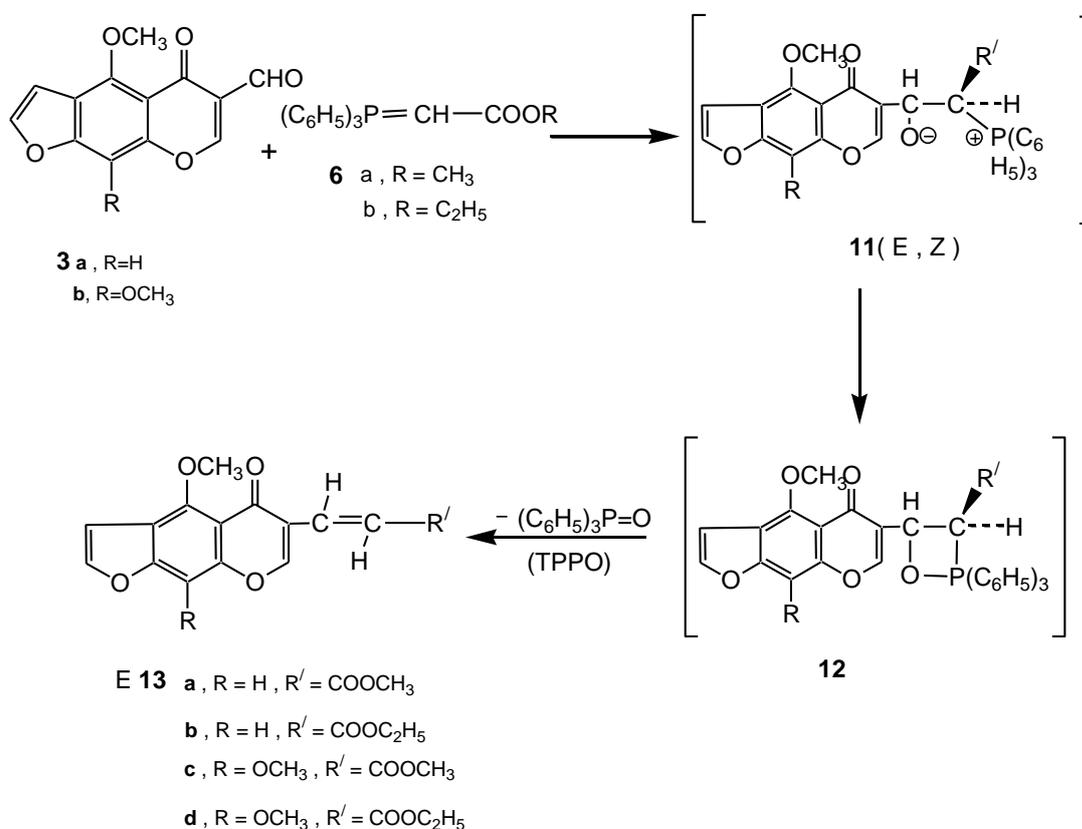
Dialkyl phosphites **4a-c** attack the aldehydic carbonyl carbon of **3a** and **3b** yielding the corresponding α -hydroxyphosphonates **10a-f**. The same products were equally obtained and identified by reacting compound **3a** with the appropriate trialkyl phosphites **5a-c** in the presence of a catalytic amount of acetic acid. Compounds **10** regenerate the starting γ -pyrone derivatives **3a** or **3b** and the appropriate dialkyl phosphite **4** upon thermolysis under reduced pressure (**Scheme 2**).



- 10 a**, R = H ; R' = CH₃
b, R = H ; R' = C₂H₅
c, R = H ; R' = C₃H_{7-i}
d, R = OCH₃ ; R' = CH₃
e, R = OCH₃ ; R' = C₂H₅
f, R = OCH₃ ; R' = C₃H_{7-i}

Scheme 2

The reaction of **3a,b** with stabilized ylidenetriphenylphosphoranes **6a,b** was also investigated. When **3a** and **3b** were allowed to react with one mole equivalent of carbomethoxy- **6a** and/or carbethoxymethylenetriphenylphosphorane **6b** in boiling dry toluene, the respective 6-carbalkoxyethylenes **13a, b, c, d** were obtained. Triphenylphosphine oxide (TPPO) was also isolated and identified (m.ps, mixed m.ps and comparative IR spectra) in each reaction. Carrying out the same reactions using two mole equivalents of the Wittig reagent **6** led to the same results (**Scheme 3**).

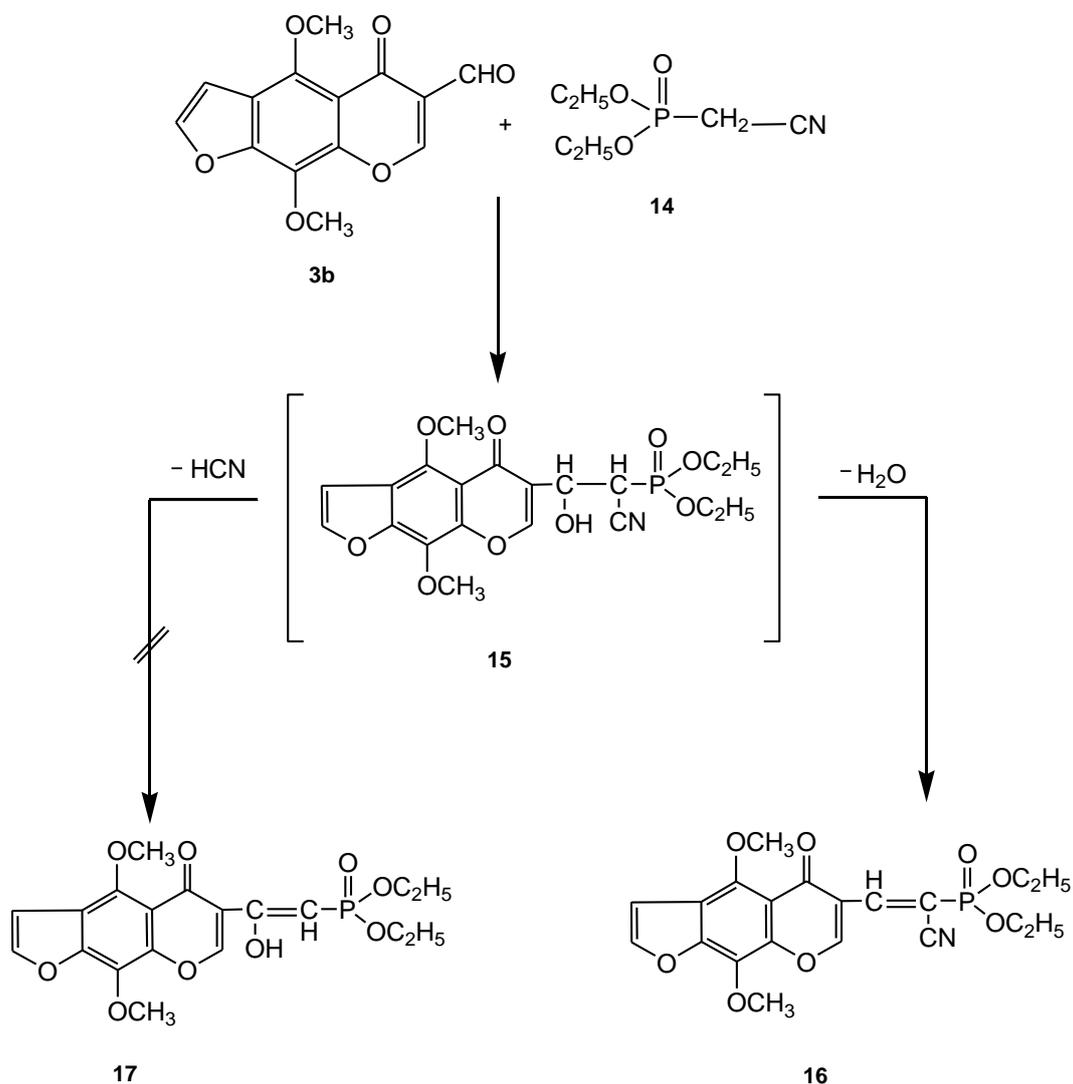


Scheme 3

Compounds **13** can present in the *Z* or *E* configuration. However, the *E* isomer seems to be the only structure that represents ethylenes **13**. In favour of this conclusion is the large coupling constant ($J_{\text{HH}} > 17 \text{ Hz}$) between the two hydrogens of the exocyclic AB-system in their ¹H-NMR spectra. Moreover, *E* selective carbonyl olefination is generally accepted for the reactions of aldehydes with stabilized Wittig reagents of type **6**.

To compare the behavior of **3b** towards Horner-Wittig reagents, its reaction with diethyl cyanomethylphosphonate **14** was investigated. Upon conducting the reaction in dry toluene, a white substance was isolated and formulated as 6-[(α -cyano- α -diethoxyphosphoryl)ethylidenyl]-4,9-dimethoxy-5-oxo-5H-furo[3,2-g] benzopyran **16** (**Scheme 4**).

Compatible analytical and spectroscopic (IR, ^1H NMR, ^{13}C NMR, ^{31}P NMR and mass) measurements were gained for the new products.

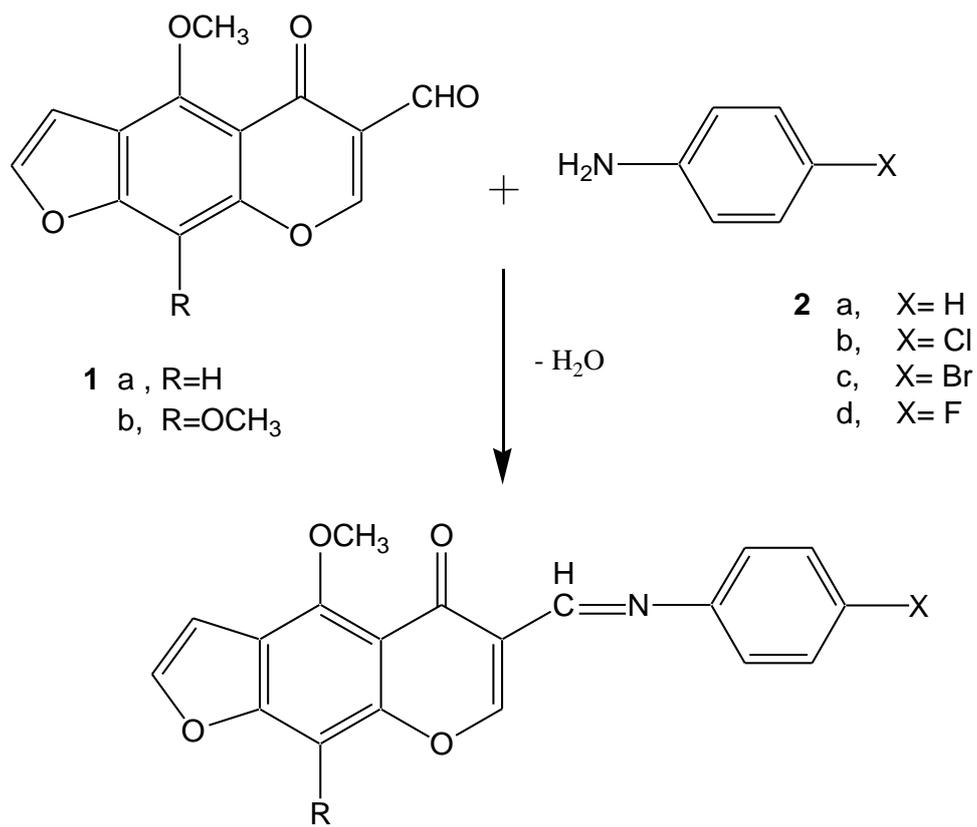


Scheme 4

Part II

Preparation of 6-(Aryliminomethyl)furobenzopyran-5-ones and Studying their Reactions with Dialkyl Phosphites.

The starting materials, namely 4-methoxy-5-oxo-5H-furo[3,2-g][1]-6-(phenyliminomethyl)benzopyran **3a** and 4,9-dimethoxy-5-oxo-5H-furo[3,2-g][1]-6-(phenyliminomethyl)benzopyran **3e** in addition to their para-substituted derivatives **3b,c,d** and **3f,g,h** were essentially prepared by condensing **1a** or **1b** with the appropriate aryl amine (aniline, p-chloroaniline, p-bromoaniline and/or p-fluoroaniline) in boiling ethanol. While anils **3a,e,c** were prepared according to established procedures, monoanils **3b,d,f-h** are now prepared for the first time (Experimental) (**Scheme 1**).



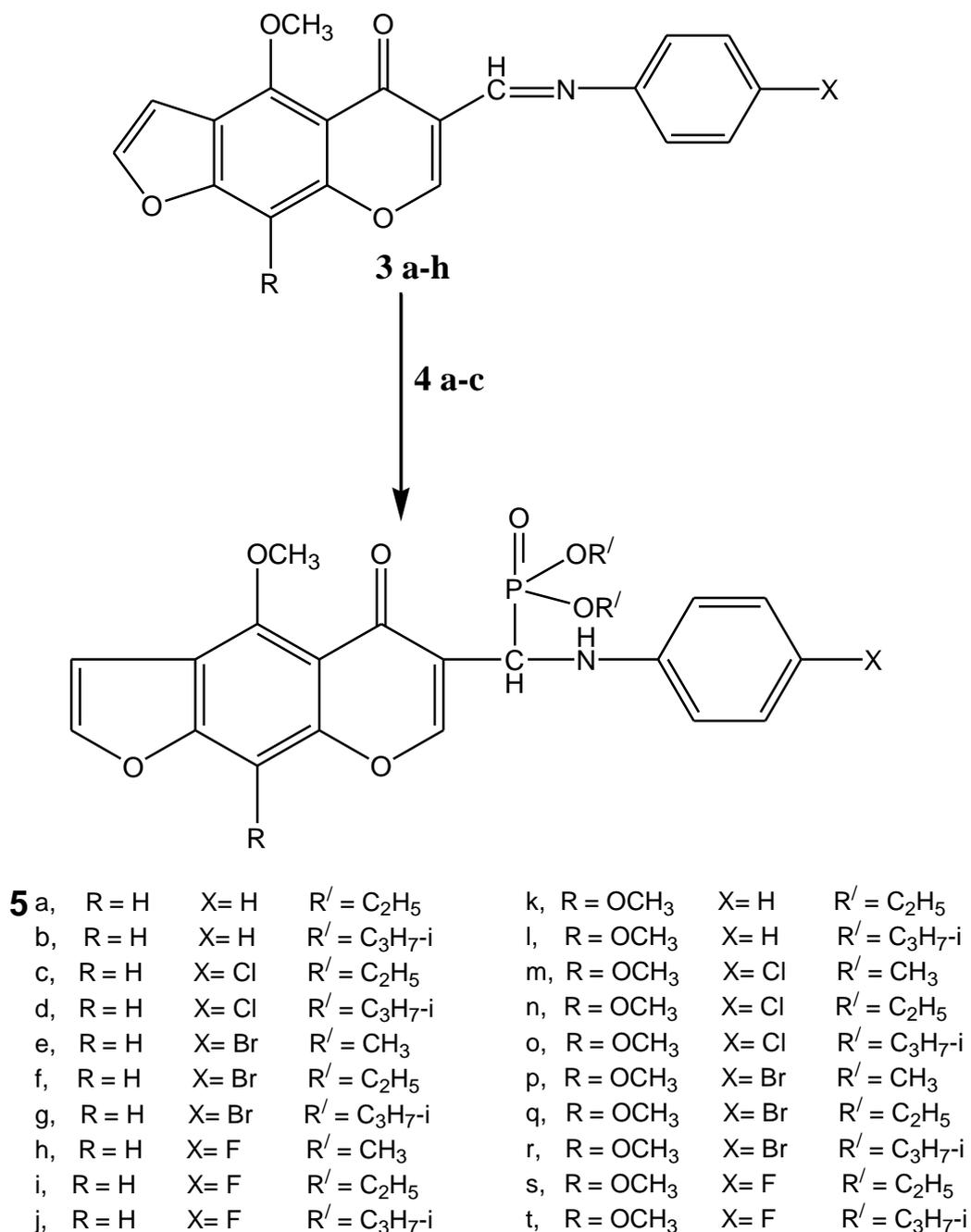
- 3 a, R¹=X=H
b, R=H X=Cl
c, R=H X=Br
d, R=H X=F
e, R=OCH₃ X=H
f, R=OCH₃ X=Cl
g, R=OCH₃ X=Br
h, R=OCH₃ X=F



- 4 a, R' = CH₃
b, R' = C₂H₅
c, R' = C₃H₇-i

Scheme 1

Monoanils **3a-h** react smoothly with the appropriate dialkyl phosphites **4a-c** at 100°C in absence of solvent to give the respective phosphonate 1:1 adducts **5a-t** in coloured crystalline forms. Compatible analytical and spectroscopic measurements were in a good accord with the assigned structures (**Scheme 2**).



Scheme 2

Upon thermolysis under reduced pressure, compound **5n** regenerated the starting material, namely 4,9-dimethoxy-5-oxo-5H-furo[3,2-g][1]-6-[p-chlorophenylimino-methyl]benzopyran **3f** and diethyl phosphite **4b**.

In terms of the Hard-Soft-Acid-Base (HSAB) principle, dialkyl phosphites **4** are considered as soft (strong) bases. Therefore, they can induce attack at the azomethine-carbon atom (the soft acid part of the -C=N- grouping in **3**) to yield **5**.

Part III

The Biological Activity of Some New Organophosphorus Compounds Against *Aphis gossypii* (Glover).

The pesticidal activities of nine selected new compounds prepared in part II were tested. Some of them showed high activity against adults of *Aphis gossypii* (Glover). The results showed that compound **5c** is the most effective followed by **5g**, **5e**, **5j** and **5p** while **5n** was the least effective.

Compounds used

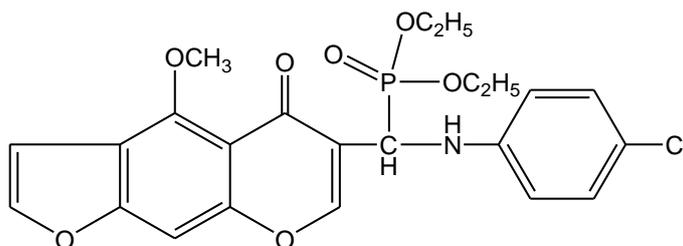
Compound: **5c**

Chemical name:

4-Methoxy-5-oxo-5H-furo[3,2-g][1]-6-[(α -diethoxyphosphoryl- α -p-chloroanilino)methyl]benzopyran

Empirical Formula: C₂₃H₂₃ClNO₇P

Structural Formula:



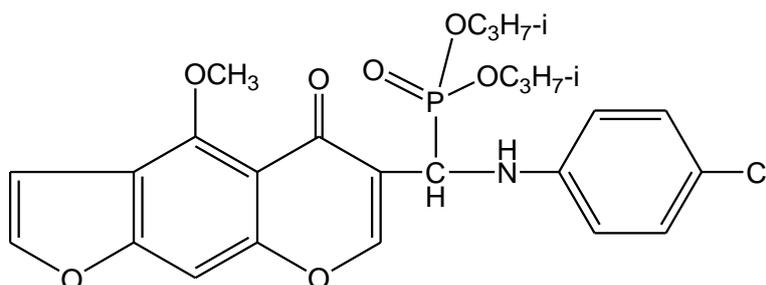
Compound: 5d

Chemical name:

4-Methoxy-5-oxo-5H-furo[3,2-g][1]-6-[(α -diisopropoxyphosphoryl- α -p-chloroanilino)methyl]benzopyran

Empirical Formula: C₂₅H₂₇ClNO₇P

Structural Formula:



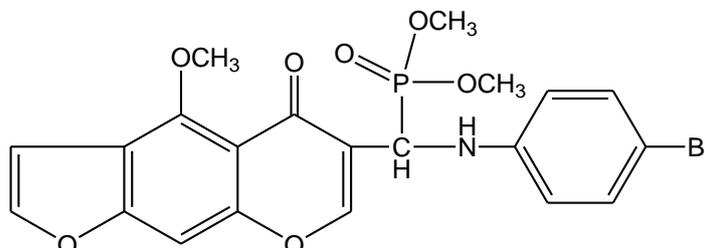
Compound: 5e

Chemical name:

4-Methoxy-5-oxo-5H-furo[3,2-g][1]-6-[(α -dimethoxyphosphoryl- α -p-bromoanilino)methyl]benzopyran

Empirical Formula: C₂₁H₁₉BrNO₇P

Structural Formula:



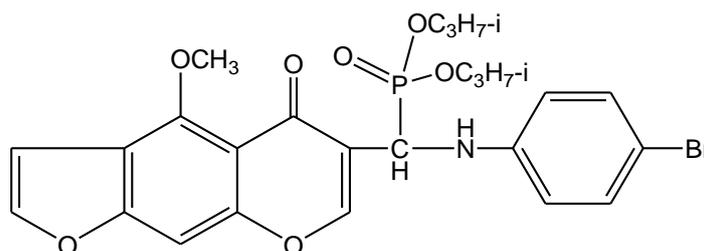
Compound: 5g

Chemical name:

4-Methoxy-5-oxo-5H-furo[3,2-g][1]-6-[(α -diisopropoxyphosphoryl- α -p-bromoanilino)methyl]benzopyran

Empirical Formula: C₂₅H₂₇BrNO₇P

Structural Formula:



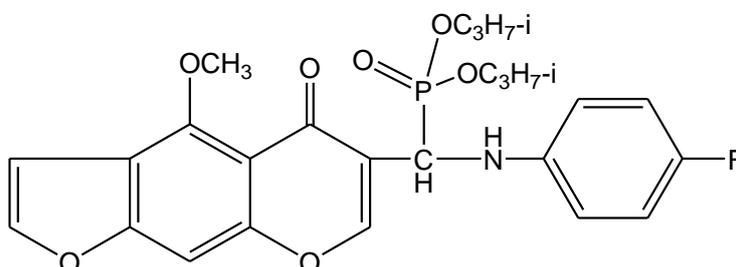
Compound: 5j

Chemical name:

4-Methoxy-5-oxo-5H-furo[3,2-g][1]-6-[(α -diisopropoxyphosphoryl- α -p-fluoroanilino)methyl]benzopyran

Empirical Formula: C₂₅H₂₇FNO₇P

Structural Formula:



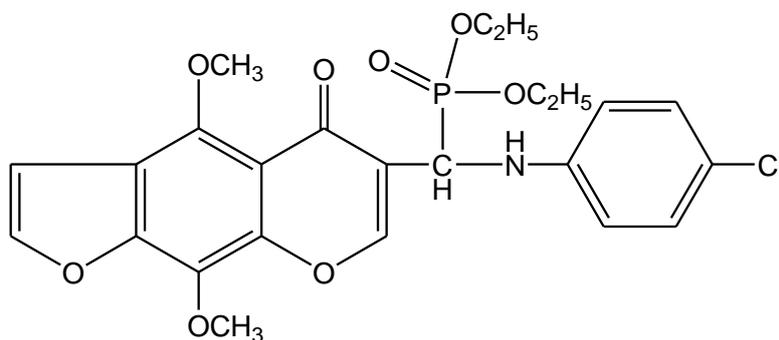
Compound: 5n

Chemical name:

4,9-Dimethoxy-5-oxo-5H-furo[3,2-g][1]-6-[(α -diethoxyphosphoryl- α -p-chloroanilino)methyl] benzopyran

Empirical Formula: C₂₄H₂₅ClNO₈P

Structural Formula:



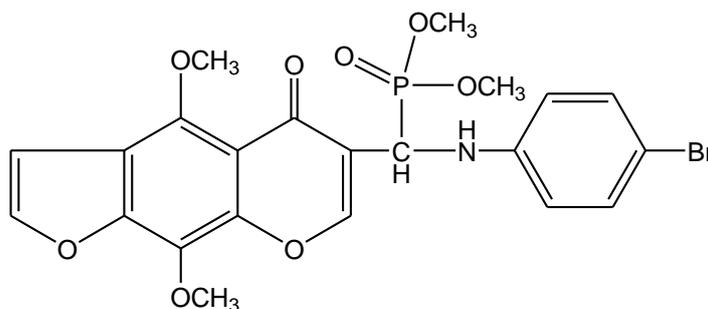
Compound: 5p

Chemical name:

4,9-Dimethoxy-5-oxo-5H-furo[3,2-g][1]-6-[(α -dimethoxyphosphoryl- α -p-bromoanilino)methyl] benzopyran

Empirical Formula: C₂₂H₂₁BrNO₈P

Structural Formula:



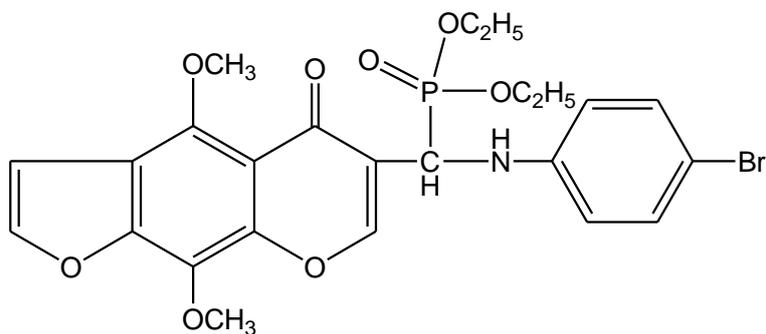
Compound: 5q

Chemical name:

4,9-Dimethoxy-5-oxo-5H-furo[3,2-g][1]-6-[(α -diethoxyphosphoryl- α -p-bromoanilino)methyl] benzopyran

Empirical Formula: C₂₄H₂₅BrNO₈P

Structural Formula:



Compound: 5t

Chemical name:

4,9-Dimethoxy-5-oxo-5H-furo[3,2-g][1]-6-[(α -diisopropoxyphosphoryl- α -p-fluoroanilino)methyl] benzopyran

Empirical Formula: C₂₆H₂₉FNO₈P

Structural Formula:

