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ORGANOPHOSPHORUS CHEMISTRY, PART 37: SYNTHESIS AND INSECTICIDAL ACTIVITIES OF SOME PHOSPHONATE ADDUCTS DERIVED FROM 6-(ARYLIMINOMETHYL)-FUROBENZOPYRAN-5-ONES

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Dialkyl phosphites attack 6-(Aryliminomethyl)furobenzopyran-5-ones at the imine-carbon atom to give new phosphonate 1:1 adducts. The obtained compounds regenerate the starting materials upon thermolysis under reduced pressure. Structures of the new products were attested by compatible analytical and spectroscopic measurements. Insecticidal activity tests assured that some new compounds show marked potency against adults of Aphis gossypii (Glover), which infests cotton crops.

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Keywords 6-(Aryliminomethyl)furobenzopyran-5-ones; insecticidal activities; phosphorylation; spectroscopic evidence; thermolysis

INTRODUCTION

Phosphonates have become very important compounds by virtue of their recognition and efficiency as reagents in organic syntheses as well as for their biological and industrial importance.[1,2] Aldehydes,[3–6] aldimines,[7–10] and ketimines[11–14] are suitable substrates for the preparation of members of this class of compounds. Recently,[1] we have reported on the reaction of 4-methoxy- (**1a**) and 4,9-dimethoxy-5-oxo-5H-furo[3,2-g]benzopyran-6-carboxaldehyde (**1b**) with dialkyl phosphites and trialkyl phosphites.[1] This, together with our growing interest in the organophosphorus chemistry of arylimines derived from carbonyl compounds,[7,8,11–13,15,16] has initiated us to study the behavior of monoarylimines **3a–h** towards dialkyl phosphites **4a–c**.

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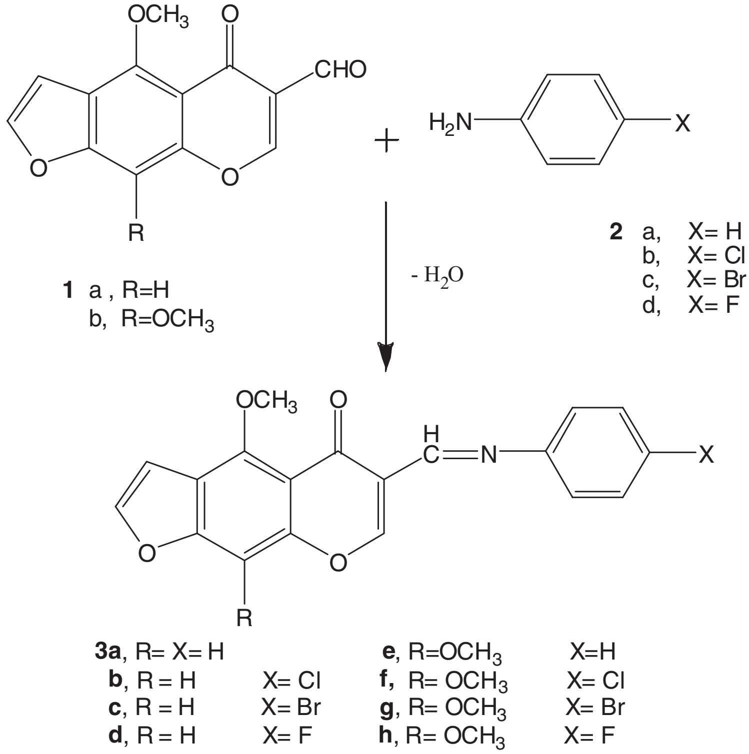
RESULTS AND DISCUSSION

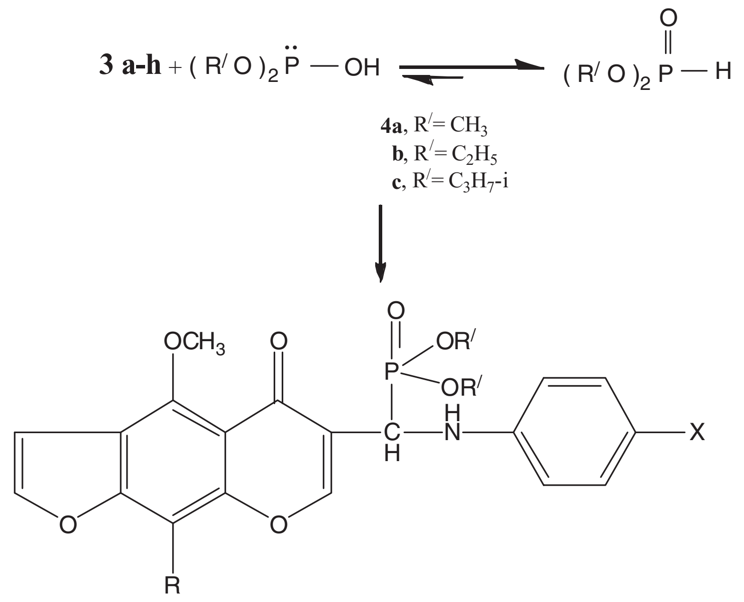
Arylimines **3a–h** of the present study were essentially prepared by condensing **1a** or **1b** with the appropriate aryl amine (aniline, p-chloroaniline, p-bromoaniline, and/or p-fluoroaniline) in boiling ethanol. While anils **3a**, **c**, and **e** were prepared according to established procedures,[17,18] monoanils **3b**, **d**, and **f–h** are now prepared for the first time (see the Experimental section and Scheme 1).



Scheme 1

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

Thus, microanalysis and molecular weight determination (MS) for 4,9-dimethoxy-5-oxo-5H-furo[3,2-g][1]-6-[(α-diethoxyphosphoryl-α-p-chloroanilino)methyl] benzopyran **5n**, taken as a representative example, corresponded to $C_{24}H_{25}ClNO_8P$. A positive chemical shift at $\delta = 22.68$ ppm was recorded in the ^{31}P NMR spectrum of **5n** (vs. 85% H_3PO_4), confirming the presence of a phosphorus-to-carbon linkage (phosphonate group)[19] in its structure. The IR spectrum of **5n** (KBr, cm^{-1}) revealed the presence of strong absorption bands at 3293 (NH, free), 1644 (C=O, γ-pyrone), 1605, 1537 (C=C, furan and aromatic), 1280 (P=O, free),[20] and 1050 (P—O—C_2H_5).[20] The strong (C=N) band present in the IR spectrum of monoanil **3f** at 1611 was absent in the spectrum of **5n.** The ^1H NMR spectrum of **5n** (DMSO-d_6, δ ppm) showed protons of the ethoxy-CH_3 groups attached to

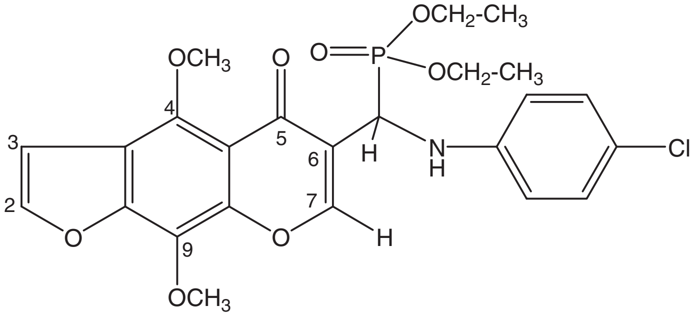


5	R	X	R/
a	R = H	X= H	R/ = C_2H_5
b	R = H	X= H	R/ = C_3H_7-i
c	R = H	X= Cl	R/ = C_2H_5
d	R = H	X= Cl	R/ = C_3H_7-i
e	R = H	X= Br	R/ = CH_3
f	R = H	X= Br	R/ = C_2H_5
g	R = H	X= Br	R/ = C_3H_7-i
h	R = H	X= F	R/ = CH_3
i	R = H	X= F	R/ = C_2H_5
j	R = H	X= F	R/ = C_3H_7-i
k	R = OCH_3	X= H	R/ = C_2H_5
l	R = OCH_3	X= H	R/ = C_3H_7-i
m	R = OCH_3	X= Cl	R/ = CH_3
n	R = OCH_3	X= Cl	R/ = C_2H_5
o	R = OCH_3	X= Cl	R/ = C_3H_7-i
p	R = OCH_3	X= Br	R/ = CH_3
q	R = OCH_3	X= Br	R/ = C_2H_5
r	R = OCH_3	X= Br	R/ = C_3H_7-i
s	R = OCH_3	X= F	R/ = C_2H_5
t	R = OCH_3	X= F	R/ = C_3H_7-i

Scheme 2

phosphorus (6H) as two triplets (each with $^4J_{HP} = 9.00$ H_Z) at 1.08 and 1.22. Apparently, the asymmetry of the molecule due to the presence of a stereocenter would render the two ethoxy groups distereotropic, and hence anisochronous, thus resulting in the observed splitting pattern.[21–23] The expected two quintets due to protons of the ethoxy-CH_2- groups attached to phosphorus (4H) appeared as an obscured multiplet (10H) in the 4.18–3.83 region, wherein two singlets emerge at 4.10 (3H, OCH_3) and 4.00 (3H, OCH_3). The spectrum also showed two doublets (each with $J_{HH} = 9$ H_Z) due to protons of the $-N-C_6H_4-Cl$ grouping (AB-system, 4H) at 6.70 (2H) and 7.12 (2H), as well as two doublets (each with $J_{HH} = 2.5$ H_Z) at 8.40, 8.15 due to the furan ring protons. Signals were also found at 7.30 (1H, γ-pyrone, s), 5.20 (1H, dd, each with $^2J_{HH} = 18$ H_Z, for P-$\underline{CH}$-NH), and at 6.45 (1H, NH, diffused multiplet, D_2O—exchangeable). The main features of the ^{13}C NMR spectrum of **5n** (DMSO, δppm) are the presence of signals at 174.49 (C=O), 62.98 (C4 $O\underline{C}H_3$), 62.88(C9 $O\underline{C}H_3$), 62.63 (P-O-$\underline{C}H_2$-), 62.53 (P-O-$\underline{C}H_2$-), 61.86 (P-O-C-$\underline{C}H_3$), 61.34 (P-O-C-$\underline{C}H_3$), 16.28(P-$\underline{C}$H), 105.28(C3), and 146.10(C2).

Moreover, structure **5n** has been exclusively and unambiguously assigned based on X-ray crystallographic analysis. An ORTEP projection of single X-ray diffraction of



5n

compound **5n** is shown in Figure 1. The compound is clearly seen to be a phosphonate adduct, resulting from the attack by diethyl phosphite on the C=N bond where the phosphoryl moiety is oriented *anti* with respect to the arylamino group. Crystal data and experimental parameters used for the intensity data collection strategy and final results of the structure determination of compound **5n** are represented in Table I. Selected bond lengths (Å) and bond angles (deg) are shown in Tables S1 and S2, respectively (see the Supplemental Materials, available online).

In the mass spectrum of compound **5n**, the molecular ion peak (**a**, M^+) was hardly conspicuous at m/z 521, 1.69% (523, 0.41%), showing its relative instability under electron

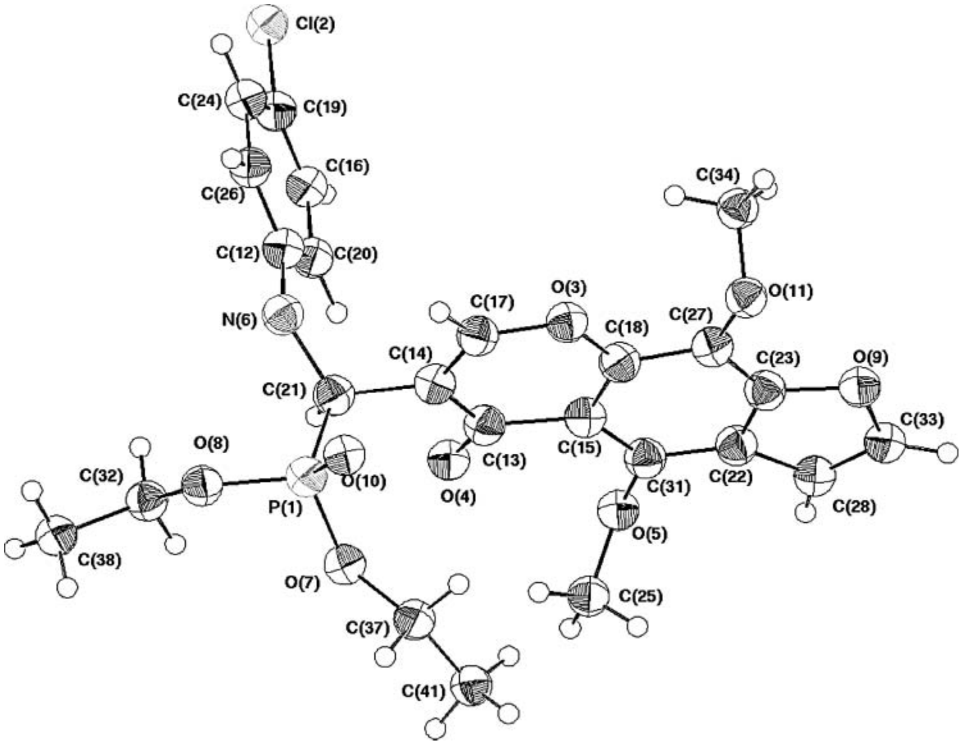


Figure 1 ORTEP projection of single X-ray diffraction of compound **5n**.

Table I Crystal structure and data refinement parameters of compound **5n**

Compound	**5n**
Empirical formula	$C_{24}H_{25}ClNO_8P$
Formula weight	521.890
Crystal system / space group	Triclinic/P1
a / Å	10.9425 (10)
b / Å	11.8380 (11)
c / Å	13.168 (2)
α / °	82.430 (4)
β / °	69.323 (4)
γ / °	64.873 (11)
V / Å^3	1444.5 (3)
Z	2
D $_{calc}$ (g/cm^3)	1.200
μ (mm^{-1})	0.23
Color / shape	Colorless / needles
Temp (K)	298
Theta range for collection	2.910–21.967
Reflections collected	3513
Independent reflections	2985
Data/restraints/parameters	1314/0/346
Goodness of fit on F^2	2.228
Final R indices [$I > 2\sigma(I)$]	0.081
R indices (all data)	0.156

bombardment. Cleavage of M^+ at axis x produces the base peak (cation **b**) at m/z 384, which ejects a neutral CH_2O molecule from one of the methoxyl groups to give ion **c** at m/z 354 (356) (Scheme S1, Supplemental Materials). Upon thermolysis under reduced pressure, compound **5n** regenerated the starting materials, 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,[24–26] dialkyl phosphites **4** are considered to be soft bases. Therefore, they can induce attack at the azomethine-carbon atom to yield **5**.

INSECTICIDAL ACTIVITY

Pesticidal activities are associated with a variety of organophosphorus compounds,[27–30] which are liable to become less effective as a result of building cross-resistance in pests. Therefore, continuous efforts are devoted towards developing new generations of these pesticides. This initiated us to study the effect of some selected new phosphonate adducts (**5c**, **d**, **e**, **g**, **j**, **n**, **p**, **q**, and **t**) against *Aphis gossypii* (Glover) (see the Supplemental Materials available online). This sucking aphid pest infests cotton crops worldwide. It affects cotton yield by direct feeding and fiber quality by excreting honeydew, which supports growth of harmful microorganisms.[31] The slide-dip method[32,33] was used in this study. The average mortality percentage was calculated per each concentration and was corrected using Abbott's formula[34] if necessary. The corrected percentage mortality rate of each compound was statistically computed.[35]

CONCLUSION

Results of the present study offer a new group of phosphonates (**5a–t**) derived from furochromones, to which belong many biologically active principles frequently used as drugs.[36,37] They also belong to the pharmacologically interesting α-aminophosphonates.[38–41] The new compounds were prepared by allowing monoanils **3a–h** to condense with the appropriate dialkyl phosphites **4**. The study also clearly shows that the γ-pyrone carbonyl group in substrates **3** show marked stability towards attack by the examined phosphorus reagents, at least under the prevailing experimental conditions. The phosphonate adduct **5c** showed marked pesticidal activity against *Aphis gossypii* (Glover), which infests cotton crops.

EXPERIMENTAL

Reactions with dialkyl phosphites were carried out under an atmosphere of dry argon. Solvents were purified and dried according to usual procedures. Dialkyl phosphites are commercially available (Aldrich) and were freshly distilled before use. Compounds **3a**,[17] 3c,[17] and **3e**[18] were prepared according to known procedures. Melting points were recorded on an Electrothermal melting point apparatus and were uncorrected. The infrared spectra were obtained from KBr-disks using a Brüker Vector 22 (Germany) Infrared Spectrophotometer and/or a Jasco FT/IR-300E Fourier transform infrared spectrophotometer and reported in cm^{-1}. ^{1}H NMR spectra were recorded on a Varian Mercury VX-300 Spectrometer (at 300 MHz) and/or a Jeol JNM-EX 270 FT Spectrometer (at 270 MHz). Proton chemical shifts (δ) are reported in ppm downfield from TMS. ^{13}C NMR spectra were recorded on a Jeol JNM-EX 270 FT Spectrometer (at 68 MHz). ^{31}P NMR spectra were recorded on JNM ECA-500 Spectrometer (*vs* 85% H_3PO_4) at 200 MHz. Mass spectra were recorded on a Finnigan SSQ 7000 Spectrometer and/or a Shimadzu GC MS-Q 1000 EX spectrometer at 70 eV. The microanalyses were carried out at the Microanalytical Unit, Cairo University, Cairo, Egypt. Intensity data collection for X-ray diffraction was performed with a Kappa-CCD Enraf Nonius FR 590 Single Crystal Diffractometer. The structures were solved by direct methods using the *SIR*92 program[42] and refined using ma*X*us.[43] The molecular graphics were made with ORTEP.[44] Crystallographic data (CIF) for the structures reported in this article have been deposited in the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication No. 757276. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB 12EZ, UK. (FAX: + 44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk).

Preparation of Monoanils 3b,d and 3f–h

A mixture of **1a** (or **1b**) (0.005 mol) in ethanol and aryl amine **2**a (or **2b,c** and **d**) (0.005 mol) in ethanol was heated under reflux until no more of the reactants could be detected (TLC). The reaction mixture was left at room temperature overnight, and the yellow solid obtained was filtered off and recrystallized from ethanol.

4-Methoxy-5-oxo-5H-furo[3,2-g][1]-6-(p-chlorophenyliminomethyl)benzo pyran (3b). Yield 95%, mp 118–120°C; IR (KBr): 3162.7 (CH, aromatic), 2939.0, 2883.9 (CH, aliphatic), 1650.0 (C=O, γ-pyrone), 1618.8(C=N), 1592.7, 1560.4(C=C, aromatic) cm^{-1}. Anal. Calcd. (%) for $C_{19}H_{12}ClNO_4$ (353.76): C, 64.51, H, 3.42, Cl, 10.02, N, 3.96; Found (%): C, 64.34, H, 3.65, Cl, 10.22; N, 3.86; MS: m/z (%) 353.20 (M^+, 20.50), 355.20 (M^+, 7.98).

4-Methoxy-5-oxo-5H-furo[3,2-g][1]-6-(p-bromophenyliminomethyl)benzopyran (3c). Yield 92%, mp 144–146°C. ^{13}C NMR (DMSO, δ ppm): 180.54 (*C*=O), 144.74 (*C*=N) and 60.76 (O*C*H$_3$). Anal. Calcd. (%) for $C_{19}H_{12}BrNO_4$ (398.21): C, 57.31; H, 3.04; Br, 20.07; N, 3.52; Found (%): C, 57.11; H, 3.12; Br, 19.91; N, 3.47.

4-Methoxy-5-oxo-5H-furo[3,2-g][1]-6-(p-fluorophenyliminomethyl)benzopyran (3d). Yield 95%, mp 170–171°C; IR (KBr): 3158.1 (CH, aromatic), 2973.3, 2942.8 (CH, aliphatic), 1649.6(C=O, γ-pyrone), 1616.3 (C=N), 1590.2, 1564.0(C=C, aromatic) cm^{-1}. Anal. Calcd. (%) for $C_{19}H_{12}FNO_4$ (337.31): C, 67.66, H, 3.59, F, 5.63, N, 4.15; Found (%): C, 67.45, H, 3.79, F, 5.73, N, 3.95; MS m/z (%): 337.00 (M^+, 22.90).

4,9-Dimethoxy-5-oxo-5H-furo[3,2-g][1]-6-(p-chlorophenyliminomethyl) benzopyran (3f). Yield 95%, mp 162–164°C; IR (KBr): 3136.4 (CH, aromatic), 2968.5, 2927.4 (CH, aliphatic), 1646.8(C=O, γ-pyrone), 1611.9(C=N), 1592.9, 1477.8 (C=C, aromatic) cm^{-1}; Anal. Calcd. (%) for $C_{20}H_{14}ClNO_5$ (383.79): C, 62.59, H, 3.68, Cl, 9.24, N, 3.65; Found (%): C, 62.69, H, 3.42, Cl, 9.34, N, 3.45; MS m/z (%): 383.40 (M^+, 2.05), 385.40 (M^+, 0.58).

4,9-Dimethoxy-5-oxo-5H-furo[3,2-g][1]-6-(p-bromophenyliminomethyl) benzopyran (3g). Yield 90%, mp 172–174°C; IR (KBr): 3303.8 (CH, aromatic), 2970.2, 2934.5 (CH, aliphatic), 1650.5(C=O, γ-pyrone), 1609.1(C=N), 1583.1, 1557.7 (C=C, aromatic) cm^{-1}; Anal. Calcd. (%) for $C_{20}H_{14}BrNO_5$ (428.24): C, 56.09, H, 3.30, Br, 18.66, N, 3.27; Found (%): C, 56.29, H, 3.45, Br, 18.50, N, 3.07; MS m/z (%) : 427.21 (M^+, 12.81).

4,9-Dimethoxy-5-oxo-5H-furo[3,2-g][1]-6-(p-fluorophenyliminomethyl) benzopyran (3h). Yield 90%, mp 168–170°C; IR (KBr): 3125.9 (CH, aromatic), 2970.8, 2940.0 (CH, aliphatic), 1651.8 (C=O, γ-pyrone), 1605.9 (C=N), 1594.9, 1565.4 (C=C, aromatic) cm^{-1}. Anal. Calcd. (%) for $C_{20}H_{14}FNO_5$ (367.33): C, 65.40, H, 3.84, F, 5.17, N, 3.81; Found (%): C, 65.63, H, 3.94, F, 4.98, N, 3.62; MS: m/z (%) 366.91 (M^+, 81.08).

Reaction of 3a–h with Dialkyl Phosphites 4a–c

A mixture of **3**a (or **3b–h**) (0.005 mol) and DAP **4a** (**4b** or **4c**) was heated in the absence of solvent at 100°C until no more of the reactants could be detected (TLC). After removing the volatile materials in vacuo, the residual substance was collected and recrystallized from the appropriate solvent to give the respective phosphonates (**5a–t**). As an example, the characterization of **5a** is presented here. (**5b–5t** are given in the Supplemental Materials, available online.)

4-Methoxy-5-oxo-5H-furo[3,2-g][1]-6-[(α-diethoxyphosphoryl-α-anilino) methyl]benzopyran (5a). Yield 90%, mp 160–162°C (ethanol, dark yellow); IR (KBr): 3318.9 (NH), 1643.0 (C=O), 1228.4 (P=O), 1036.5 (P—O—Et) cm^{-1}. ^1H NMR (DMSO-d$_6$) 1.13, 1.23[6H, P—(O—C—C*H*$_3$)$_2$, 2t], 3.95–4.10[4H, P-(O—C*H*$_2$—C)$_2$, m], 4.15[3H, OC*H*$_3$,s], 5.28–5.32[1H, P-C-*H*, dd $^2J_{HP}$ = 23.43], 6.14[1H, P—C—N*H*, bs D_2O-exchangeable], 6.76–7.10[5H, aromatics, m], 7.29[1H for γ-pyrone ring, s], 7.53[1H, benzene ring, s], 8.05, 8.38 ppm [2H, for furan ring, 2d, J_{HH} = 2.18]; ^{31}P NMR(DMSO) 24.6 ppm; Anal. Calcd. (%) for $C_{23}H_{24}NO_7P$ (457.42) : C, 60.39, H, 5.29, N, 3.06, P, 6.77. Found (%): C, 60.12, H, 5.28, N, 2.96, P, 6.51; MS: m/z (%) 457(M^+, 5.13), 320 (M^+-•P(O)(OC$_2$H$_5$)$_2$, 100).

Degradation Experiment: Thermolysis of Phosphonate 5n

The phosphonate adduct **5n** (0.2 g), taken as a representative example, was heated in a cold finger sublimator at 200°C (bath temperature) under reduced pressure (1 mm/Hg) for 1 h. The reaction vessel was left to cool, and the compound that sublimed was collected and recrystallized from ethanol to give yellow crystals, mp 162–164°C, and was proved to be **3f** (mp, mixed mps, and comparative IR spectra). The drops that collected at 40°C gave the violet color reaction described for diethyl phosphite with 3,5-dinitrobenzoic acid in the presence of an alkali.[45]

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