

FUSED PHOSPHONO SUBSTITUTED O-, AND N-HETEROCYCLES VIA CONDENSATIVE CYCLISATION REACTIONS OF α -PHOSPHONYL CARBANIONS WITH 4-THIAZOLIDINONES

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*Phosphono substituted-thiazolones **5a,b** together with fused phosphono-pyran-5-ones **9a,b** and the diolefins **8a–d** were regioselectively prepared in reasonable yields from the reactions of 5-arylidene-4-thiazolidinones **1a,b** with phosphonoacetates **2a,b**. Conversely, Michael addition products **11a,b** (~30%) along with the phosphono substituted-thiazole derivatives **12a,b** (~33%) were obtained from treating **1a,b** with cyanomethylenephosphonates (**2c**). The reactions of **1a,b** with vinylphosphonate **2d** proceeded with phase-transfer catalysis, yielding the corresponding 2-thioalkyl-derivatives **14a,b** and phosphonates **13a,b**.*

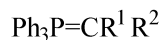
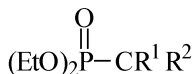
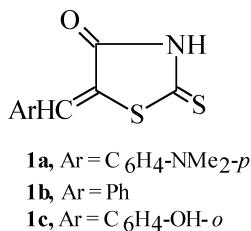
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Thiazolidinones have been recently exploited as herbicides, acaricides, and insecticides, in which many compounds have commercially been produced.¹ The biological activity, to a large degree, is attributed to the nature of the substituent in the thiazolidine ring. In fact, it has been shown that the phosphonyl group could regulate important biological functions of the substrate.² Thus, it is conceivable that molecular modification of thiazole rings by introducing organophosphorus functionality is likely to reveal potential pesticide activity. Although some synthetic approaches to phosphonyl thiazolidinones have been reported,³ there is still much active research in this area.

In a series of articles from this laboratory, we reported⁴ on the synthesis and reactions of new phosphono substituted-heterocycles starting from the inexpensive and easily accessible α -phosphonyl carbanions. This article describes the results of our studies on the

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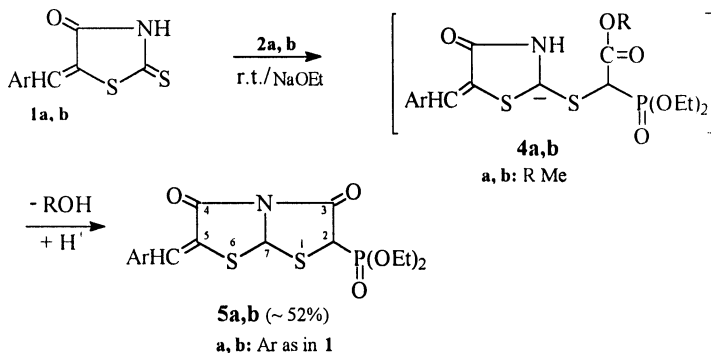
preparation and reactions of novel phosphono substituted-heterocycles derived from the reactions of thioxothiazolidinones **1a,b** with different types of α -phosphonyl carbanion **2a–d**. Similarities and differences in the reactivity of phosphonates **2** and phosphorane counterparts **3** toward 4-thiazolidinones **1** are also discussed.



RESULTS AND DISCUSSION

When 5-arylmethylene-2-thioxo-4-thiazolidinone **1a** (also known as 5-arylidine-rhodanines¹) was treated with an excess of diethyl phosphonoacetates **2a,b** in alcoholic sodium methoxide solution at room temperature, the reaction was not complete even after 3 days. The product mixture was then subjected to column chromatography to give in each case, a colored solid (~52%) together with an unchanged substrate **1a** (~20%). This product, for which the structure of diethyl [5-arylmethylene-3,4-dioxo-3,4*H*-2,7-dihydrothiazolo[8,7-*c*]thiazol-2-yl] phosphonate **5a** was proposed, was the only one produced regardless of the ratio of the reactants employed. Similar treatment of **1b** with the phosphonates **2a,b** afforded the phosphonate analog **5b** (58%) and an unchanged **1b** (18%). However, in all cases, **2a,b** were utilized in three-fold molar excess, compared to the corresponding **1a,b**, in order to obtain reasonable yields. Similar fused-thiazole derivatives to **5** are, however, known in the literature.^{1b,5}

Mass spectra and elemental analyses of **5a,b** indicated that the reaction results in a 1:1 condensative cyclisation accompanied by extrusion of the appropriate alcohol molecule (Scheme 1). Structure **5** ($\delta_p = \sim 19.3$ ppm) was, however, established on the basis of IR and NMR spectra. Thus, each of the products exhibited a carbonyl group, similar to that of the starting substrate **1** ($\nu \sim 1698$ cm⁻¹). The ¹H NMR spectra showed a common one-proton singlet near δ 7.8 ppm assignable to the vinylic proton resonance. The starting thiazolidinones **1** exhibited such a signal at $\delta_H = \sim 7.83$ ppm. On the other hand, the ¹³C NMR⁶ spectra of **5** (in CDCl₃) showed the absence of a thiocarbonyl carbon atom (C=S) at ~ 195 ppm. Instead, the two carbonyl-carbon atoms in **5** gave two



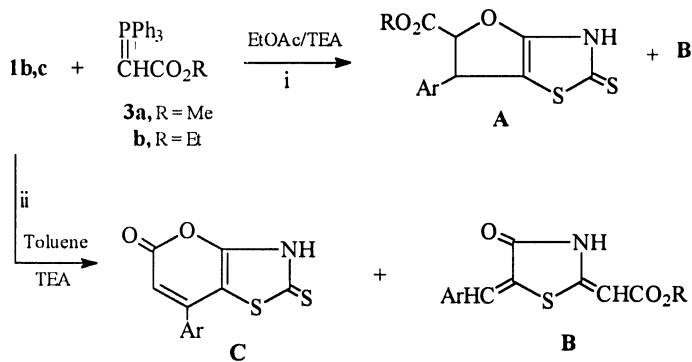
SCHEME 1

signals around ~ 160 ppm. The phosphonate-carbon atom (C–P) signal was observed at ~ 48 ppm (d, $^1J_{C-P} = \sim 187$ Hz) in the ^{13}C NMR of **5**. These values coincide with the chemical shift expected for a ring sp^3 -carbon atom bearing a phosphonyl moiety as indicated by the large coupling constant.

The foregoing results confirm the assigned structure **5** and rule out the alternative structure **9** (Scheme 2). Consequently, the studied reaction is site selective leading, under the prevailing experimental conditions, to the exclusive formation of **5a,b**. Similar thiophilic addition by carbanions at the =S are known.^{7,8} Furthermore, considering the interesting parallel between the chemistry of phosphonyl and phosphonium ylides, similar observation were previously reported for the reaction of alkylidenephosphoranes with thiocarbonyl compounds,^{7,8} as well as for the reactions of alkyl phosphites with thiobenzophenones and others.⁹

When the above reaction (**1a,b** + **2a,b**) was carried out at reflux temperatures, we observed that the diolefins **8a–d** and the phosphonates **9a,b** were isolated in almost equal yields ($\sim 30\%$) together with a low yield of **5** ($\sim 12\%$). The oxidation of **9a,b** with *N*-bromosuccinimide (NBS), in carbon tetrachloride containing a catalytic amount of dibenzoyl peroxide, led to the formation of the dehydrogenated products **10a,b** ($\sim 62\%$) (Scheme 2). Elemental analyses, molecular weight measurement (MS), IR and NMR spectroscopy (see Experimental section) all have confirmed the structures of the new products.

The reaction mechanisms illustrated in Schemes 1 and 2 are postulated as follows: thiophilic addition of the phosphonyl carbanion **2** to thiazolidinone **1** yields the intermediate **4**. At low temperature, the latter undergoes intramolecular cyclisation giving the fused thiazolone **5** via elimination of the appropriate alcohol molecule and protonation from the solvent (Scheme 1). However, at relatively high temperature,



SCHEME 3

intermediate **7**, which can readily lactonizes to give **9** upon alkylation and displacement of an ROH molecule (Scheme 2). *N*-Alkylation process meets a well documented analogy in the reaction of Horner reagent with quinonimines,¹¹ pyrroles,^{12a} nitrosonaphthols,^{12b} and oximes.^{4b}

It was reported^{3a} that phosphite esters attack 4-thiazolidinones **1**, preferably, at the exocyclic ethylene bond by 1:2 addition to give the corresponding phosphorylated compounds. On the other hand, the formation of a fused pyrone as described in Scheme 2 parallel the reactions of 5-alkylidene thiazolidine-2,4-thiones with alkenes.^{13a} Furthermore, we have reported^{13b} an analogous mechanism for the reaction of 5-arylidinerhodanines **1b,c** with alkylidenephosphorane counterparts **3a,b** (Scheme 3).

Thus, by applying alkoxycarbonylmethylenetriphenylphosphoranes **3a,b** on **1b,c** in refluxing ethyl acetate, and in the presence of triethylamine (TEA), conjugated dihydrofuro[2,3-*d*]-thiazole-2*H*-thiones **A** (~46%) together with the diolefins **B** (~18%) were isolated. Carrying out the reaction in refluxing toluene, and also in the presence of TEA, led to the formation of the fused pyrone derivative **C** (~52%) and **B** (~11%).

Obviously, the mechanisms outlined in Schemes 2 and 3 show a similar initial attack for the phosphonyl and phosphorane ylides **2** and **3**. However, the transformations are quite different. The main difference between the present reaction and the corresponding one of the Wittig reagents with the same substrate **1b**^{13c} is that, in the latter case, the formation of the products is accompanied by elimination of the phosphorus moiety. The contrasting behavior of the initial intermediate through elimination “of the phosphorus moiety” is because Ph₃P is a much better leaving group than [(EtO)₂PO⁻]. There is much precedence for this difference.⁷ The results also showed the activated

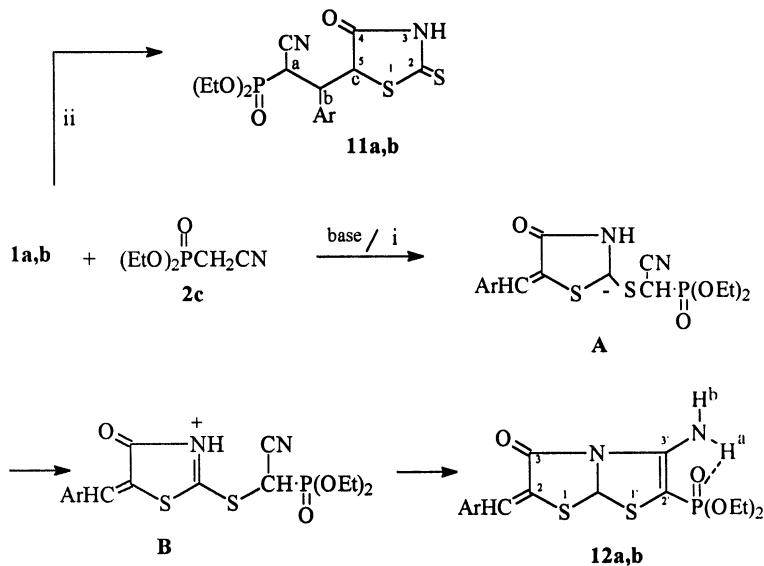
carbon-carbon double bond is a preferable site of attack by the phosphorane ylides, whereas the thiocarbonyl group is the preferable one with phosphonyl carbanions.

Next, we investigated the reaction of **1a,b** with diethyl cyanomethylenephosphonate (**2c**). In contrast to the transformations described above, when **1a,b** and **2c** (three-fold molar excess compared to **1**) reacted in boiling dimethylformamide (DMF) containing LiH (2 equiv., compared to **2c**), conjugated products **11a,b** (~27% yield) and the fused-thiazole derivatives **12a,b** (~40% yield) were obtained.

Elemental analyses and spectral data substantiated the chemical structures of **11** and **12**. The ^1H NMR spectra of the compounds **11a,b** showed a sharp singlet of the NH proton at ~ 9.44 . There were still three types of CH protons [$\delta(\text{H}^a) \sim 2.8$ ppm (dd (m), 1H), $\delta(\text{H}^b) \sim 3.5$ ppm (dd (m), 1H) and $\delta(\text{H}^c) \sim 4.5$ (dd, (m), 1H)]. The C(O) carbon signal in the ^{13}C NMR spectra was observed at δ_{C} 161–163 ppm, while the carbon atom of the CN group was shown at about 117 ppm. The 1-C atom gave a doublet at about 44 ppm ($^1J_{\text{C,P}} \sim 136$ Hz). The C(S)-carbon signal in the ^{13}C NMR spectra was observed by 192–194 ppm. In the IR spectra of **11**, the CN-group was located at 2220, 2218 as a weak band and the thione-function was given at $\sim 1190\text{ cm}^{-1}$ as a strong sharp band.

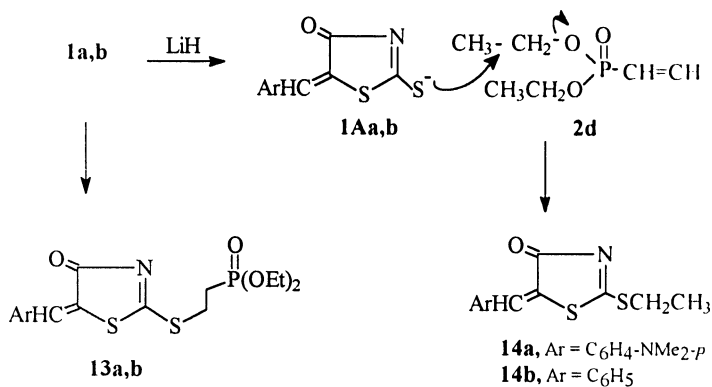
The ^1H NMR spectrum of **12a** ($\delta_{\text{p}} = 24.16$ ppm) showed two types of the NH_2 -protons [$\delta(\text{H}^a) = 6.55$ (sbr, 1H) and $\delta(\text{H}^b) = 9.71$ (s br., 1H)]. The different chemical shifts of the NH_2 -protons are the spectroscopic evidence for the presence of intramolecular hydrogen bonds between one of the hydrogens of the NH_2 -protons and the oxygen atom of the P=O bonding in the phosphonate group. The 2-C atom in the ^{13}C NMR appeared as a doublet at 97.2 ($^1J_{\text{C,P}} = 196.3$ Hz). Compounds **12** were presumably formed through the attack of sulfur on **2c** to generate the intermediate **B** via the intermediate **A**. Subsequent cyclisation and transformation of the cyano group led directly to the formation of fused thiazole derivative **12** (Scheme 4). Obviously, the driving force for the latter step can be attributed to the substitution on the methine carbon atom with electron withdrawing thiol-, cyano- and phosphonato-groups, which results in an increased acidity of the corresponding methine proton. Similar observation has been previously reported.¹⁴

Treatment of **1** with diethyl vinylphosphonate (**2d**) in DMF, in the presence of LiH, yielded the phosphonates **13** (~43% yield) and the S-alkylated products **14a,b** (~26 yield) (Scheme 5). The product **14b** is, however, identical, in all aspects, to the known¹⁵ 5-benzylidene-2-(ethylthio)thiazolidin-4-one. Obviously, compound **13** is the product of addition of the electron rich thioxo S-atom of either **1a,b** or its conjugate base on the electrophilic beta position of O,O-diethyl vinylphosphonate



SCHEME 4

2d (which behaves like an unsaturated carboxylic ester), as has been previously discussed.^{1b,16} On the other hand, **14a,b** resulted from direct alkylation (using the ethyl phosphonate as the alkylating agent) on the sulfide anion intermediate $-\text{S}^-$ **1A** that resulted from treatment of **1a,b** with LiH. This type of alkylation is well known in organophosphorus chemistry.^{8,9}



SCHEME 5

CONCLUSION

The results of the present and the previous work^{13b} point out the variety of reaction pathways, which can follow an initial attack of phosphorus ylides **2** and **3** to C=S and the exocyclic-C=C groups in 5-arylidine-2-thioxothiazolidin-4-ones **1a–b**. Desulfuration process is also observed in some products (see **8**, Scheme 2 and **B**, Scheme 3). Finally, the present work describes an efficient and simple approach to the synthesis of a variety of condensed phosphono substituted *O*-, *N*-, and *S*-heterocycles in reasonable yields. This general method consists of suitable applications of the appropriate phosphonyl carbanion to thiazolidinones. Data on the pharmaceutical potency of the new compounds **5**, **8–10**, and **11–13** will be published elsewhere.

EXPERIMENTAL

Melting points are uncorrected. Infrared spectra were measured with a Perkin-Elmer IR-spectrometer Model 597 using KBr discs. The ¹H and ¹³C NMR spectra were recorded with a Bruker Model WH-270 MHz spectrometer. The ³¹P NMR spectra were run on a Varian CFT-20 relative to external H₃PO₄. Mass spectra were performed at 70 eV on a Schimadzu GCS-QPEX spectrometer provided with a data system. All reactions were carried out under strictly moisture and oxygen free conditions. Light petroleum refers to the fraction 40–60°C.

I. Treatment of 5-Arylmethylene-2-thioxothiazolidinones **1a,b** with Diethyl Phosphonoacetates (**2a,b**)

(A) Preparation of **5a**

A 6 molar solution of sodium ethoxide (NaOEt) in absolute ethyl alcohol solution (25 mL) was treated with a 3 molar solution of methyl diethyl phosphonoacetate (**2a**) and then 4-thiazolidinone **1a**¹⁸ (0.8 g, 3 mmol, 1 molar amount) was added. The resulting reaction mixture was kept stirring for 3 days at room temperature. The product mixture was concentrated and diluted with a small amount of distilled water followed by solvent extraction (CHCl₃) and drying. Then the solvent was evaporated in the presence of 7 g (Kieselgel 60, particle size 0.2–0.5 mm; E. Merck, Darmstadt) and packed with n-hexane. Elution with hexane/CHCl₃ (8:2, v/v) afforded red crystals of diethyl [5-(4'-dimethylaminophenylmethylene)-3,4-dioxo-3,4H-6,8-thiazolo-[8,7-c]-2,7-dihydro-1,8-thiazol]-2-yl-phosphonate (**5a**) (0.7 g, 52%), m.p. 168–170°C (from MeCN). (Found: C, 48.74; H, 5.18;

N, 6.25; P, 7.12; S 14.41. $C_{18}H_{23}N_2O_5PS_2$ requires C, 48.85; H, 5.24; N, 6.33; P, 7.00; S, 14.49%; $\nu_{\max}(\text{KBr})\text{cm}^{-1}$ 1698, 1690 (3-C=O & 4-C=O), 1622 (C=C, exocyclic), 1245 (P=O), 1100 (P-O-C); $\delta_H(270\text{ MHz; CDCl}_3)$: 1.08, 1.32 (6H, 2dt, J_{H-H} 6.6, $^4J_{H-P}$ 3.8, H_3C-C-O), 3.06, 3.08 [6H, 2s, (H_3C)₂N], 4.16, 4.24 (4H, 2dq, J_{H-H} 6.6, $^3J_{H-P}$ 4.6, $2 \times H_2CO$), 4.48 (1H, dd, J_{H-P} 17.5, 2-CHP), 5.13 (1H, dd, J_{H-H} 2.7, J_{H-P} 4.4, 7-C-H), 7.36 (2H, m, $H-C_6H_4$), 7.61 (2H, m, $H-C_6H_4$), 7.79 (1H, s, 5-C=CH); $\delta_C(270\text{ MHz; CDCl}_3)$: 14.6, 15.2 ($2CH_3-C-O$), 31.2, 35.4 [$(CH_3)_2N$], 48.8 (d, J_{C-P} 187.8, 2-C-P), 55.7 (7-C), 61.2, 62.5 ($2 \times CH_2O$), 120.9, 122.4, 126.4, 131.7 (6C, C_6H_4), 158.2, 161.5 ($2 \times C=O$); $\delta_P(\text{CDCl}_3)$ 19.4 ppm; m/z (EI) (%): 442 (M^+ (36), requires 442.5), 427 (13), 414 (10), 398 (22), 386 (30), 305 (55), 252 (100). The second fraction (1:1, v/v) afforded red leaflets of unchanged substrate **1a** (180 mg, 22%), m.p. 285–288°C (EtOH) (Lit.,¹⁷ m.p. 285°C); m/z (%) found 264 (100) $C_{12}H_{12}N_2OS_2$ requires 264.36. Similarly, the reaction of triethyl phosphonoacetate (**2b**) with thiazolidinone **1a** was performed at r.t. for 3 days in ethanol containing NaOEt, whereby the procedure was the same with **2a** using the same amounts. After the usual workup, phosphonate **5a** (660 mg, 50%), m.p. 168–170°C (MeCN) was isolated and was shown to be identical to material prepared above on using **2a**.

(B) Preparation of **5b**

A mixture of **1b**¹⁸ (0.8 g, 3.62 mmol) and the appropriate Wittig-Horner synthon **2a** or **2b** (~10 mmol) in absolute EtOH (25 mL) containing NaOEt (~20 mmol) was stirred for 3 days at r.t. After the usual workup, the product residue was column chromatographed (silica gel/hexane with increasing amounts of $CHCl_3$ to give, in each case, only **5b** along with unchanged **1b** (~20%). Diethyl (5-benzylidene-3,4-dioxo-3,4H-6,8-thiazolo[8,7-c]-2,7-dihydro-1,3-thiazol-2-yl-phosphonate (**5b**) was obtained (8:2, v/v) as yellow crystals (830 mg, 58%), m.p. 146–148°C (from benzene). (Found: C, 48.18; H, 4.46; N, 3.43; P, 7.87; S, 16.12. $C_{16}H_{18}NO_5PS_2$ requires C, 48.11; H, 4.54; N, 3.51; P, 7.75; S, 16.05%; $\nu_{\max}(\text{KBr})\text{cm}^{-1}$ 1700, 1687 (3-C=O & 4-C=O), 1628 (C=C, exocyclic), 1240 (P=O), 1105 (P-O-C); $\delta_H(270\text{ MHz; CDCl}_3)$: 1.09, 1.32 (6H, 2dt, J_{H-H} 6.6, J_{H-P} 3.6, $2 \times H_3C-C-O$), 4.17, 4.24 (4H, 2dq, J_{H-H} 6.6, J_{H-P} 4.4, $2 \times H_2CO$), 4.58 (1H, dd, J_{H-H} 2.4, J_{H-P} 15.8, 2-CH-P), 5.16 (1H, dd, J_{H-H} 2.4, J_{H-P} 4.4, 7-C-H), 7.36 (3H, m, $H-C_6H_5$), 7.61 (2H, m, $H-C_6H_5$), 7.78 (1H, s, 5-C=CH); $\delta_C(270\text{ MHz; CDCl}_3)$: 14.3, 15.7 ($2CH_3-C-O$), 48.4 (d, J_{C-P} 187.8, 2-C-P), 56.5 (7-C), 61.3, 62.4 ($2 \times CH_2O$), 120.3, 121.8, 124.6, 131.8 (6C, C_6H_5), 159.1, 160. ($2 \times C=O$); $\delta_P(\text{CDCl}_3)$ 20.1 ppm; m/z (EI) (%): 399 (M^+ (36), requires 399.43), 397 (44), 371 (18), 343 (32), 262 (100).

(C) Preparation of 8a, b, 9a, and 5a

A mixture of **1a** (0.8 g, 3 mmol) and **2a** or **2b** (9 mmol) in absolute EtOH containing NaOEt (~20 mmol) was refluxed for 24 h. After the usual workup, the residue was chromatographed with hexane/CHCl₃ to give **8a**, **5a**, and **9a** or **8b**, **5a**, and **9a** respectively.

i. With 2a. Dimethyl 2-[(5-(4-dimethylaminophenylmethylene)-4-oxo-4H-1,3-thiazole]-1,2-ethylenedicarboxylate (**8a**) was obtained (9:1, v/v) as red crystals (400 mg, 30%), m.p. 110–112°C (from diethyl ether). (Found: C 57.82, H 4.07, N 7.43, S 8.67. C₁₈H₁₈N₂O₅S requires C 57.74, H 4.85, N 7.48, S 8.56%); $\nu_{\max}$ (KBr)/cm⁻¹ 1705–1692_w (3 × C=O), 1618, 1634 (2 × C=C, exocyclic); δ_{H} (270 MHz; CDCl₃): 2.99, 3.01 [6H, 2s, (H₃C)₂N], 3.84, 3.92 (2 × 3H, 2s, 2 × H₃CO₂C), 6.97 (s, 1H, HC=CO₂Me), 7.39 (2 × 2H, 2m, H–C₆H₄), 7.56 (2H, m, H–Ar), 7.78 (1H, s, =HC–Ar); δ_{C} (270 MHz; CDCl₃): 30.8, 35.8 [(CH₃)₂N], 53.4, 55.1 (2 × CH₃O, esters), 98.7 (=CHCO₂Me), 120.6, 122.8, 126.8, 131.7 (6C, C₆H₄), 135.3 (2-C), 141.2 (=CHAr), 159.3, 160.1, 162.6 (3 × C=O); *m/z* (EI) (%): 374 (M⁺, 22), requires 374.42), 359 (11), 344 (18), 331 (50), 330 (68), 316 (9), 288 (33), 232 (100), 77 (10). The next fraction (8:2, v/v) afforded red crystals of **5a** (170 mg, 13%), m.p. 168–170°C (from MeCN), identical with the material prepared as described above.

The third fraction (7:3, v/v) yielded orange needles of 2-thioxo-2, H-N-ethyl-1,3-thiazolo-[8,9-b]-7-(4'-dimethylaminophenyl)-5-oxo-5H-6, 7-dihydropyran-6-yl)phosphonic acid diethyl ester (**9a**) (410 mg, 29%), m.p. 144–146°C (from cyclohexane). (Found: C 51.13, H 5.72, N 5.83, P 6.64, S 13.57. C₂₀H₂₇N₂O₅PS₂ C, 51.05; H, 5.78; N, 5.95; P, 6.58; S, 13.62 %); $\nu_{\max}$ (KBr)/cm⁻¹ 1738 (C=O, pyrone), 1180 (C=S), 1066 (P–O–C); δ_{H} (270 MHz; CDCl₃): 1.48 (3H, t, *J*_{H–H} 6.9, H₃C–C–N), 1.12, 1.27 (6H, 2t, *J*_{H–H} 6.5, *J*_{H–P} 4.82, H₃C–C–O–P), 2.98, 3.01 [6H, 2s, (H₃C)₂N], 4.13, 4.24 (4H, 2dq, *J*_{H–H} 6.6, *J*_{H–P} 5.2 Hz, 2 × H₂CO), 4.56 (2H, q, *J*_{H–H} 6.9, H₂CN), 5.15 (1H, d, *J*_{H–P} 4.6, *J*_{H–P} 16.6, 6-CH–P), 5.36 (1H, dd, *J*_{H–H} 4.6, *J*_{H–P} 4.8, 7-CH–Ar), 7.24, 7.67 (2 × 2H, 2m, H–C₆H₄); δ_{C} (270 MHz; CDCl₃): 11.6, 15.5, 16.2 (CH₃-C.N, CH₃-C–O–P), 30.2, 34.8 [(CH₃)₂N], 46.8 (7–C), 51.2 (CH₂.N), 62.5 (CH₂O), 73.1 (d, *J*_{C–P} 196.3, 6-CH–P), 112.9, 118.6, 126.4, 131.7 (6C, C₆H₄), 128.5 (8-C), 155.2 (9-C), 175.4 (C=O, pyrone), 193.2 (C=S); δ_{P} (CDCl₃) 21.3 ppm; *m/z* (EI) (%): 470 (M⁺(16), requires 470.55) 468 (38), 440 (8), 439 (21), 436 (15), 424 (66), 331 (100), 287 (73).

ii. With 2b. Diethyl 2-[(5-(4'-dimethylaminophenylmethylene)-4-oxo-4H-1,3-thiazole]-1,2-ethylenedicarboxylate (**8b**) was obtained (9:1, v/v) as red crystals (460 mg, 28%), m.p. 102–104°C (from pentane). (Found: C 59.77, H 5.57, N 6.88, S 7.98. C₂₀H₂₂N₂O₅S requires C 59.69, H 5.51, N 6.96, S 7.96%]; $\nu_{\max}$ (KBr)/cm⁻¹ 1700–1696 (3 × C=O), 1628, 1632

($2 \times \text{C}=\text{CHAr}$); δ_{H} (270 MHz; CDCl_3): 0.85, 0.88 (2t, 6H, $J_{\text{H-H}} = 6.5$ Hz, $\text{H}_3\text{C}-\text{C}-\text{O}$, esters), 2.97, 3.02 [6H, 2s, (H_3C) $_2\text{N}$], 3.82, 3.96 ($2 \times$ 2H, 2q, $J_{\text{H-H}} = 7.2$, H_3CO , esters), 7.0 (s, 1H, $\text{HC}=\text{CO}_2\text{Et}$), 7.29 (2H, m, $\text{H}-\text{C}_6\text{H}_4$), 7.56 (2H, m, $\text{H}-\text{C}_6\text{H}_4$), δ_{C} (270 MHz; CDCl_3): 13.8, 15.2 ($\text{CH}_3-\text{C}-\text{O}$, esters), 31.3, 36.2 [(CH_3) $_2\text{N}$], 55.3, 57.6, ($2 \times \text{CH}_2\text{O}$, esters), 103.7 ($=\text{CHCO}_2\text{Et}$), 121.3, 124.2, 126.4, 131.4 (6C, C_6H_4), 136.3 (2-C), 138.7 ($=\text{CHAr}$), 158.7, 160.4, 162.3 ($3 \times \text{C}=\text{O}$); m/z (EI) (%): 402 (M^+ (45), requires 402.47), 383 (13), 359 (42), 354 (20), 292 (60), 232 (100), 77 (17).

The second fraction (8:2, v/v) yielded red crystals of **5a** (180 mg, 14%), m.p. 168–170°C (MeCN), and shown to be identical with the material that obtained before. The third fraction (7:3, v/v) gave orange needles, which shown to be **9a** (425 mg, 30%), m.p. 144–146°C (from cyclohexane).

(D) Preparation of **8c,d**, **9b**, and **5b**

In the same manner, the reaction mixture of the appropriate carbanion **2a** or **2b** and **1b** (0.8 g, 3.6 mmol) was heated at reflux temperature for 24 h; the procedure and the workup were the same (with **1a**) using the same amounts. The residue was purified by chromatography on silica gel using hexane- CHCl_3 to give compounds **8c**, **5b**, and **9b** or **8d**, **5b**, and **9b** respectively.

i. With **2a**. Dimethyl 2-[(5-(phenylmethylene)-4-oxo-4H-1,3-thiazole]-1,2-ethylene-dicarboxylate (**8c**) was obtained (9:1, v/v) as yellow crystals (560 mg, 33%), m.p. 103–105°C (from light petroleum). (Found: C 58.16, H 3.89, N 4.11, S 9.69. $\text{C}_{16}\text{H}_{13}\text{NO}_5\text{S}$ requires C 58.00, H 3.95, N 4.23, S 9.67%; ν_{max} (KBr)/ cm^{-1} 1715, 1705, 1695 ($3 \times \text{C}=\text{O}$), 1616, 1630 ($2 \times \text{C}=\text{C}$, exocyclic); δ_{H} (270 MHz; CDCl_3): 3.61, 3.64 ($2 \times$ 3H, 2s, $2 \times \text{H}_3\text{CO}$, esters), 7.07 (s, 1H, $\text{HC}=\text{CO}_2\text{Me}$), 7.32 (3H, m, $\text{H}-\text{C}_6\text{H}_5$), 7.64 (2H, m, $\text{H}-\text{C}_6\text{H}_5$), 7.79 (1H, s, $=\text{HC}-\text{Ph}$); δ_{C} (270 MHz; CDCl_3): 53.4, 55.1 ($2 \times \text{CH}_3\text{O}$, esters), 112.3 ($=\text{CHCO}_2\text{Et}$), 120.6, 122.8, 126.8, 131.7 (6C, C_6H_5), 136.8 (2-C), 141.5 ($=\text{CHAr}$), 159.3, 160.1, 162.2 ($3 \times \text{C}=\text{O}$); m/z (EI) (%): 331 (M^+ (28), requires 331.35), 316 (12), 301 (25), 273 (19), 254 (48), 245 (16), 189 (100). The second fraction (8:2, v/v) yielded yellow crystals of **5b** (145 mg, 10%), m.p. 146–148°C (from benzene).

The third fraction (7:3, v/v) gave yellow crystals of 2-thioxo-2, H-N-ethyl-1,3-thiazolo-[8,9-b]-7-phenyl)-5-oxo-5H-6,7-dihydropyran-6-yl) phosphonic acid diethyl ester (**9b**) (420 mg, 27%), m.p. 118–120°C (from cyclohexane). (Found: C, 50.63; H, 5.11; N, 3.16; P, 7.29; S, 15.07. $\text{C}_{18}\text{H}_{22}\text{NO}_5\text{PS}_2$ requires C, 50.57; H, 5.19; N, 3.27; P, 7.25; S, 15.0%; ν_{max} (KBr)/ cm^{-1} 1735 ($\text{C}=\text{O}$, pyrone), 1245 ($\text{P}=\text{O}$), 1190 ($\text{C}=\text{S}$), 1080 ($\text{P}-\text{O}-\text{C}$); δ_{H} (270 MHz; CDCl_3): 0.89 (3H, t, $J_{\text{H-H}} = 6.9$, $\text{H}_3\text{C}-\text{C}-\text{N}$),

1.12, 1.26 (6H, 2t, J_{H-H} 6.5, $^4J_{H-P}$ 4.1, $H_3C-C-O-P$), 4.12, 4.23 (4H, 2q, J_{H-P} 10.2, H_2C-O-P), 4.75 (q, 2H, J_{H-H} 6.9, H_2C-N), 5.23 (1H, d, J_{H-P} 4.6, J_{H-P} 16.6, 6-CH-P), 5.39 (1H, dd, J_{H-H} 4.6, J_{H-P} 4.8, 7-CH-Ar), 7.38 (3H, m, $H-C_6H_5$), 7.64 (2H, m, $H-C_6H_5$); δ_P ($CDCl_3$) 16.8 ppm; m/z (EI) (%): 427 (M^+ (15), requires 427.48), 425 (41), 397 (8), 496 (23), 393 (13), 288 (100), 259 (61).

ii. With 2b. Diethyl 2-[(5'-(phenylmethylene)-4-oxo-4H-1,3-thiazole]-1,2-ethylene-diacetate (**8d**) was obtained (9:1, v/v) as yellow crystals (540 mg, 30%), m.p. 98–100°C (from pentane). (Found: C 60.21, H 3.95, N 3.81, S 6.44. $C_{18}H_{17}NO_5S$ requires C 60.15, H 4.76, N 3.90, S 8.92%); ν_{max} (KBr)/ cm^{-1} 1717, 1710, 1700 (3 $\times$ C=O), 1616, 1624 (2 $\times$ C=C, exocyclic); δ_H (270 MHz; $CDCl_3$): 0.86, 0.92 (6H, 2t, J_{H-H} 6.9, H_3C-C-O , esters), 3.85, 3.87 (4H, 2q, J_{H-H} 6.9, H_2CO , esters), 7.12 (s, 1H, $HC=CO_2Et$), 7.36 (3H, m, $H-C_6H_5$), 7.6 (2H, m, $H-C_6H_5$), 7.78 (1H, s, $=HCPH$); δ_C (270 MHz; $CDCl_3$): 14.3, 15.2 (CH_3-CO , esters), 54.6, 56.2 (2 $\times$ CH_2O , esters), 112.3 ($=CHCO_2Et$), 121.3, 124.4, 126.4, 131.7 (6C, C_6H_5), 137.1 (2-C), 139.3 ($=CHAR$), 158.6, 159.4, 162.5 (3 $\times$ C=O); m/z (EI) (%): 359 [M^+ (20), requires 359.4), 330 (27), 301 (14), 272 (21), 254 (18), 245 (41), 189 (100), 77 (14).

The second fraction (8:2, v/v) afforded yellow crystals of **5b** (216 mg, 15%), m.p. 146–148°C (MeCN), identical with the material prepared as described above, on using **2a**.

The third fraction (7:3, v/v) gave yellow leaflets, which shown to be **9b** (430 mg, 28%), m.p. 118–120°C (from cyclohexane).

Conversion of **9a,b** to **10a,b**

N-Bromosuccinimide (NBS) (54 mg, 0.3 mmol) and benzoyl peroxide (7 mg, 0.04 mmol) were added to a solution of **9a** (100 mg, 0.21 mmol) or **9b** (100 mg, 0.23 mmol) in 20 mL of dry CCl_4 . The mixture was refluxed for ~3h (TLC) and filtered while hot. Evaporation of the solvent left a residue, which was triturated with a small amount of light petroleum to give the corresponding dehydrogenated derivative, **10a** or **10b**. 2-thioxo-2,4H-N-ethyl-1,3-thiazolo-[9,8-b]-7-(4'-dimethylaminophenyl)-5-oxo-5H-pyran-6-yl) phosphonic acid diethyl ester (**10a**) (62 mg, 62%), m.p. 128–130°C (from cyclohexane). (Found: C, 51.36; H, 5.31; N, 5.88; P, 6.69; S, 13.73. $C_{20}H_{25}N_2O_5PS_2$ C, 51.27; H, 5.38; N, 5.98; P, 6.61; S, 13.69%); ν_{max} (KBr)/ cm^{-1} 1742 (C=O, pyrone), 1265 (P=O), 1185 (C=S), 1068 (P-O-C); δ_H (270 MHz; $CDCl_3$): 0.86 (3H, t, J_{H-H} 6.9, H_3C-C-N), 1.13, 1.27 (6H, 2t.br, J_{H-H} 6.9, J_{H-P} 4.5, $H_3C-C-O-P$), 2.97, 3.02 [6H, 2s, (H_3C)₂N], 4.13, 4.24 (4H, 2dq, J_{H-P} 11.5, H_2C-O-P), 4.66 (2H, q, J_{H-H} 6.9, H_2C-N), 7.26, 7.65 (2 $\times$ 2H, 2m, $H-C_6H_4$); δ_P ($CDCl_3$) 22.5 ppm; m/z (EI) (%): 468 (M^+ (34), requires 468.54), 440 (9), 439 (23), 436 (14), 424 (61), 331 (100), 287 (76).

2-Thioxo-2,*H*-*N*-ethyl-1,3-thiazolo-[8,9-*b*]-7-phenyl-5-oxo-5*H*-pyran-6-yl) phosphonic acid diethyl ester (**10b**) (60 mg, 60%), m.p. 112–114°C (light petroleum). (Found: C, 50.72; H, 4.66; N, 3.14; P, 7.34; S, 15.13. C₁₈H₂₀NO₅PS₂ requires C, 50.81; H, 4.74; N, 3.29; P, 7.28; S, 15.07%); $\nu_{\max}$ (KBr)/cm⁻¹ 1748 (C=O, pyrone), 1247 (P=O), 1185 (C=S), 1090 (P–O–C); δ_{H} (270 MHz; CDCl₃): 0.87 (3H, t, $J_{\text{H-H}}$ 6.9, H₃C–C–N), 1.12, 1.27 (6H, 2t, $J_{\text{H-H}}$ 6.5, $J_{\text{H-P}}$ 4.5, H₃C–C–O–P), 4.12, 4.23 (4H, 2q, $J_{\text{H-P}}$ 11.5, H₂COP), 4.74 (2H, q, $J_{\text{H-H}}$ 6.9, H₂C–N), 7.38 (3H, m, *H*–C₆H₅), 7.64 (2H, m, *H*–C₆H₅); δ_{P} (CDCl₃) 17.3 ppm; *m/z* (EI) (%): 425 (M⁺(44), requires 425.47), 397 (10), 396 (30), 393 (18), 288 (100), 259 (58).

II. Reaction of 4-Thiazolidinones **1a,b** with Diethyl α -cyanomethylphosphonate (**2c**)

General Procedure

To a slurry of ~1 g of LiH (60% in mineral oil, washed with pentane) in a stirred solution of DMF (20 mL) was added dropwise a solution of the phosphonate **2c** (1.8 g, ~10 mmol) in 10 mL of DMF. After the evolution of H₂ had ceased, the suspension was stirred at r.t. for further 20 min and then refluxed for 1 h. The reaction mixture was cooled to r.t., and the substrate **1a** (0.8 g, 3 mmol) or **1b** (0.8 g, 3.62 mmol) was introduced all at once and the reaction mixture was refluxed for 24–36 h. The product mixture was then concentrated and the excess of LiH was quenched carefully with ice water (30 mL) followed by acidification with conc. HCl, solvent extraction (CHCl₃), drying and evaporation. Column chromatography (silica gel/hexane with increasing amounts of CHCl₃ and then recrystallization of the crude product mixture gave the pure products **11a** and **12a** or **11b** and **12b** respectively.

2-[5-(4-oxo-2-thioxo-2,4*H*-1,3-thiazolo)]-1-cyano-2-(dimethylamino-phenyl)-ethylen-1-yl-phosphonic acid diethyl ester (**11a**) was obtained (7:3, v/v) as yellow crystals (400 mg, 30%), m.p. 170–172°C (CH₂Cl₂). (Found: C, 48.86; H, 5.42; N, 9.47; P, 7.08; S, 14.47. C₁₈H₂₄N₃O₄PS₂ requires C, 48.97; H, 5.48; N, 9.52; P, 7.02; S, 14.52%); $\nu_{\max}$ (KBr)/cm⁻¹ 3200 (NH), 2222 (CN), 1700 (C=O), 1255 (P=O), 1192 (C=S), 1085 (P–O–C); δ_{H} (270 MHz; CDCl₃): 1.11, 1.24 (6H, 2dt, $J_{\text{H-P}}$ 10.2, H₃C–C–O), 2.82 (1H, dd(m), *J* 7, 12, *H*^aC–P), 2.96, 2.99 [6H, 2s, (H₃C)₂N], 3.42 (1H, dd(m), *J* 7, 4, *H*^bC–Ar), 4.08, 4.13 (4H, 2q, $J_{\text{H-P}}$ 11.8, H₂COP), 4.63 (1H, m, –CH^c), 7.36 (2H, m, *H*–C₆H₄), 7.61 (2H, m, *H*–C₆H₄), 9.48 (1H, s_w, HN); δ_{C} (270 MHz; CDCl₃): 15.3, 16.5 (CH₃–C–O–P), 31.2, 36.3 [(CH₃)₂N], 44.6 (d, $J_{\text{C-P}}$ 136.5, CH^a(CN)–P), 46.2 (CH^b–Ar), 48.9 (CH^c), 108.2 [C(CN)], 117.6 [(CN)C], 120.7, 122.2, 127.6, 131.9 (6C, C₆H₄), 160.3 (4-C=O), 190.8 (C=S); δ_{P}

(CDCl₃) = 22.7 ppm; *m/z* (EI) (%): 441 (M⁺ (14), requires 441.51), 414 (51), 412 (33), 397 (53), 370 (62), 277 (51), 275 (100), 231 (67).

2-[(4''-dimethylaminophenyl)methylene]-3-oxo-1,3-thiazolo-[5,4-*b*]-3'-amino-1', 3'-thiazol-2'-yl phosphonic acid diethyl ester (**12a**) was obtained (6:4, v/v) as orange crystals (440 mg, 33%), m.p. 212–214°C (from cyclohexane). (Found: C, 48.99; H, 5.38; N, 9.47; P, 7.08; S, 14.58. C₁₈H₂₄N₃O₄PS₂ requires C, 48.97; H, 5.48; N, 9.52; P, 7.02; S, 14.52%]; $\nu_{\max}$ (KBr)/cm⁻¹ 3240_w (NH₂), 1700 (C=O), 1628 (=CH, exocyclic), 1225 (P=O), 1126 (P–O–C); δ_{H} (270 MHz; CDCl₃): 1.14, 1.31 (6H, dt, *J*_{H–H} 6.2, *J*_{H–P} 4.2, H₃C–CC–O), 2.97, 3.05 [6H, 2s, (H₃C)₂N], 4.05, 4.27 (4H, 2q, *J*_{H–P} 11.2, H₂CO), 4.88 (1H, d, ⁴*J*_{H–P} 2.8, 7-CH), 6.55 (1H, brs, H^aN, NH₂), 7.39 (2H, m, H–C₆H₄), 7.56 (2H, m, H–C₆H₄), 7.82 (1H, s, =CHAr), 9.71 (1H, brs, H^bN, NH₂); δ_{C} (270 MHz; CDCl₃): 14.8 (CH₃C–O), 30.4, 34.6 [(CH₃)₂N], 52.6 (7-C), 63.5 (CH₂O), 97.2 (d, ¹*J*_{C–P} 196.3, 2'-C–P), 120.9, 122.1, 126.7, 133.2 (6C, C₆H₄), 156.4 (3'-C–NH₂), 162.9 (4-C=O); δ_{P} (CDCl₃) 24.16 ppm; *m/z* (EI) (%): 441 (M⁺ (42), requires 441.51), 435 (9), 413 (13), 397 (40), 304 (100), 260 (61).

2-[5-(4-oxo-2-thioxo-2,4H-1,3-thiazolo)]-1-cyano-2-phenylethylen-1-yl-phosphonic acid diethyl ester (**11b**) was obtained (8:2, v/v) as pale yellow crystals (360 mg, 25%), m.p. 152–154°C (from light petroleum). (Found: C, 48.31; H, 4.75; N, 6.97; P, 7.66; S, 16.13. C₁₆H₁₉N₂O₄PS₂ requires C, 48.23; H, 4.81; N, 7.03; P, 7.77; S, 16.09%]; $\nu_{\max}$ (KBr)/cm⁻¹ 3230 (NH), 2218 (CN), 1696 (C=O), 1256 (P=O), 1100 (P–O–C); δ_{H} (270 MHz; CDCl₃): 1.09, 1.2 (6H, 2dt, *J*_{H–P} 10.5, H₃C–C–O–P), 2.78 (1H, dd, *J* 7, 12, H^aC–P), 3.64 (1H, dd, *J* 7, 4, H^bC–Ar), 4.12, 4.22 (4H, 2q, *J*_{H–P} 11.8, H₂C–O–P), 4.82 (1H, m, –CH^c), 7.36 (3H, m, H–C₆H₅), 7.61 (2H, m, H–C₆H₅), 9.44 (1H, s_w, HN); δ_{P} (CDCl₃) 22.1 ppm; *m/z* (EI)(%): 398 (M⁺ (18), requires 398.44), 371 (48), 369 (40), 261 (100), 234 (64), 233 (68).

2-[(4''-dimethylaminophenyl)methylene]-3-oxo-1,3-thiazolo-[5,4-*b*]-3'-amino-1', 3'-thiazol-2'-yl phosphonic acid diethyl ester (**12b**) was obtained (7:3, v/v) as yellow needles (575 mg, 40%), m.p. 178–180°C (from cyclohexane). (Found: C, 48.14; H, 4.73; N, 7.12; P, 7.63; S, 16.02. C₁₆H₁₉N₂O₄PS₂ requires C, 48.23; H, 4.81; N, 7.03; P, 7.77; S, 16.09%]; $\nu_{\max}$ (KBr)/cm⁻¹ 3240_w (NH₂), 1698 (C=O), 1620 (C=C, exocyclic), 1235 (P=O), 1050 (P–O–C); δ_{H} (270 MHz; CDCl₃): 1.12, 1.25 (6H, dt, *J*_{H–H} 6.5, *J*_{H–P} 4.3, H₃C–C–O), 4.13, 4.24 (4H, 2q, *J*_{H–P} 11.8, H₂CO), 4.79 (1H, d, ⁴*J*_{H–P} 2.7, 7-CH), 6.64 (1H, brs, H^aN, NH₂), 7.36 (3H, m, H–C₆H₅), 7.61 (2H, m, H–C₆H₅), 9.72 (1H, s_w, H^bN, NH₂); δ_{P} (CDCl₃) 23.7 ppm; *m/z* (EI) (%): 398 (M⁺ (28), requires 398.44), 382 (13), 370 (19), 261 (100), 244 (22).

III. Reaction of 4-Thiazolidinones **1a,b** with Diethyl Vinylphosphonate (**2d**)

A solution of the Wittig-Horner reagent **2d** (1.1 g, ~7 mmol) and **1a** (0.6 g, 2.3 mmol) or **1b** (0.5 g, 2.3 mmol) in DMF (30 mL) was treated with LiH (500 mg) at r.t., and the system was further refluxed for 12 h. The reaction mixture was worked up as described for the reaction with **2c** and separated by column chromatography using hexane/CHCl₃ as the eluents to give the products **13a** and **14a** or **13b** and **14b** respectively.

5-(4'-Dimethylamino-phenylmethylene)-2-(ethylthio)-1,3-thiazol-4-one (14a) was obtained (9:1, v/v) as orange crystals (155 mg, 28%), m.p. 98–100°C (from cyclohexane) (Lit.¹⁴ m.p. 98°C), *m/z* (EI) (%): 292 (M⁺ (68), requires 292.42), 264 (100), 221 (67).

The phosphonate **13a** was obtained as yellow crystals (350 mg, 44%), m.p. 198–200°C (from acetone). (Found: C, 50.52; H, 5.82; N, 6.47; P, 7.35; S, 14.56. C₁₈H₂₅N₂O₄PS₂ requires C, 50.45; H, 5.88; N, 6.54; P, 7.23; S, 14.96%]; $\nu_{\max}$ (KBr)/cm⁻¹ 1700 (C=O), 1628 (C=C), 1350 (–S–C), 1255 (P=O), 1100 (P–O–C); δ_{H} (270 MHz; CDCl₃): 1.09, 1.22 (6H, 2dt, $J_{\text{H-H}}$ 7.2, $J_{\text{H-P}}$ 3.5, $\text{H}_3\text{C-C-OP}$), 2.26 (2H, dt, $^1J_{\text{H-P}}$ 18.5, H_2CP), 3.05, 3.58 [6H, 2s, (H_3C)₂N], 3.37 (2H, dt, $^3J_{\text{H-P}}$ 12, $\text{H}_2\text{C.S}$), 4.15, 4.22 (4H, 2dq, $J_{\text{H-H}}$ 7.2, $J_{\text{H-P}}$ 4.8, H_2COP), 7.37 (2H, d, $J_{\text{H-H}}$ 7.2, $\text{H-C}_6\text{H}_4$), 7.41 (2H, d, $J_{\text{H-H}}$ 7.2, $\text{H-C}_6\text{H}_4$), 7.82 (1H, s, =HCAr); δ_{C} (270 MHz; CDCl₃): 15.3, 16.1 (2 × CH₃C–O), 22.8 (d, $J_{\text{C-P}}$ 142.5, CH₂–P), 29.2 (CH₂S), 31.4, 33.7 [(CH₃)₂N], 60.4, 61.2 (CH₂O.P), 120.6, 124.9, 126.7, 128.7 (6C, C₆H₄), 139.7 (=CHAr), 143.8 (5-C, Het), 151.3 (2-C, Het), 159.7 (C=O); δ_{P} (CDCl₃) 15.8 ppm; *m/z*(EI) (%): 428 (M⁺ (27), requires 428.51), 291 (55), 247 (32), 264 (100), 220 (60).

5-Benzylidene-2-(ethylthio)-1,3-thiazol-4-one (14b) was obtained (9:1, v/v) as pale yellow needles (130 mg, 23%), m.p. 55–57°C (from pentane) (lit.¹⁵ m.p. 55°C), *m/z* (EI) (%): 249 (M⁺ (56), requires 249.35), 221 (100), 199 (18).

The phosphonate **13b** was obtained as pale yellow crystals (380 mg, 41%), m.p. 155–157°C (from benzene). (Found: C, 49.92; H, 5.29; N, 3.57; P, 8.14; S, 16.34. C₁₆H₂₀NO₄PS₂ requires C, 49.86; H, 5.23; N, 3.63; P, 8.04; S 16.63%]; $\nu_{\max}$ (KBr)/cm⁻¹ 1705 (C=O), 1622 (C=C), 1342 (S–C), 1256 (P=O), 1105 (P–O–C); δ_{H} (270 MHz; CDCl₃): 1.11, 1.32 (6H, 2dt, $J_{\text{H-P}}$ 10.5, $\text{H}_3\text{C-C-O}$), 2.31 (2H, dt, $^3J_{\text{H-P}}$ 18.5, $\text{H}_2\text{C-P}$), 3.34 (2H, dt, $J_{\text{H-P}}$ 12, $\text{H}_2\text{C-S}$), 4.17, 4.23 (4H, 2dq, $J_{\text{H-P}}$ = 11.7, $\text{H}_2\text{C-O-P}$), 7.35 (3H, m, $\text{H-C}_6\text{H}_5$), 7.64 (2H, m, $\text{H-C}_6\text{H}_5$), 7.80 (1H, s, =CHAr); δ_{C} (270 MHz; CDCl₃): 15.5, 16.1 (2 × CH₃–C–O), 24.3 (d, $^1J_{\text{C-P}}$ 143.4, CH₂–P), 28.8 (CH₂–S), 60.4, 61.2 (CH₂OP), 125.6, 129.2, 130.0, 137.7 (C–C₆H₅), 141.7 (=CHPh), 152.2 (2'-C, Het), 160.3 (C=O, Het.); δ_{P} (CDCl₃) 15.7 ppm; *m/z* (EI) (%): 385 (M⁺ (30), requires 385.44), 248 (50), 221 (100).

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