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The Behavior of 2-Thioxo-4-thiazolidinones toward Organophosphorus Reagents

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ABSTRACT: *The reaction of 2-thioxo-4-thiazolidinone (***1a***) with phosphorus ylides* **2a** *and* **2b** *afforded compounds* **5** *and* **6**. *On the other hand, formylmethylenetriphenylphosphorane (***2c***) reacts with* **1a** *and its N-methyl derivative* **1b** *to give the new complicated phosphonium ylides* **7a,b**, *respectively. Reactions of* **1b** *with ylides* **2a** *and* **2d** *gave rise to the olefinic compound* **8** *and the new phosphorane product* **9**. *Moreover, dialkyl phosphites* **3a,b** *and trialkyl phosphites* **4a–c** *react with* **1a** *to give both the alkylated products* **10a–c** *and the dimeric compounds* **11,12**. *A mechanism is proposed to explain the formation of the new products.*© 1999 John Wiley & Sons, Inc. Heteroatom Chem 10: 337–341, 1999

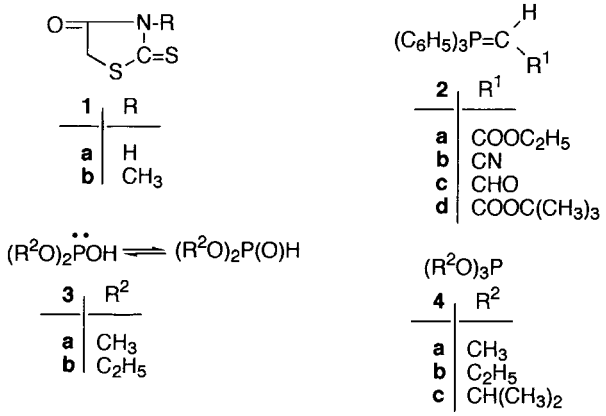
INTRODUCTION

The chemistry of thiazolidinones has received considerable attention [1–3]. Many thiazolidinone derivatives exhibit high potential biological activities, such as anticonvulsant, tuberculostatic, anti-inflammatory, and antithyroidal activities, and are used as bactericidal, pesticidal, fungicidal, and insecticidal agents [3,4]. This together with our interest in organophosphorus chemistry [5–10] enhanced the synthesis of new phosphorus compounds incorporating such important nuclei that may possibly lead to further biological activity. The present study deals with the reaction of 2-thioxo-4-thiazolidinone (rhodanine, **1a**) and its 3-methyl derivative **1b** with resonance stabilized phosphonium ylides (**2a–e**). A comparative study of the behavior of **1a** toward dialkyl phosphites **3a–b** and trialkyl phosphites **4a–c** is also reported (Scheme 1).

RESULTS AND DISCUSSION

When 2-thioxo-4-thiazolidinone (**1a**) was treated with one equivalent of ethoxycarbonylmethylenetriphenylphosphorane (**2a**) in refluxing benzene, compound **5** and triphenylphosphine oxide were isolated in good yields (Scheme 2).

Similarly, the reaction of 2-thioxo-4-thiazolidinone (**1a**) with cyanomethylenetriphenylphosphorane (**2b**) proceeds in refluxing toluene to give compound **6** in 90% yield. Triphenylphosphine oxide has also been isolated from the product mixture. The structural assignments for compounds **5** and **6** are based upon elemental and mass spectral analyses, IR, ^{1}H NMR, and ^{13}C NMR (cf. Experimental).



SCHEME 1

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The reaction of **1a** with formylmethylenetriphenylphosphorane (**2c**) has also been investigated. Treatment of **1a** with mol equivalents of **2c** in refluxing toluene leads to the formation of the new phosphonium ylide **7a** as the sole reaction product. Triphenylphosphine and triphenylphosphine oxide are neither isolated nor identified in the reaction medium (Scheme 2).

Compound **7a** possesses an ylide–phosphorane structure, since it exhibits a positive shift in its ^{31}P NMR ($\delta = +16.3$) spectrum in the region characteristic for this class of compounds [11]. On the basis of IR, ^{1}H NMR, ^{13}C NMR, MS and elemental analyses, the structure of compound **7a** was deduced (cf. Experimental). The formation of **7a** involves the condensation between the aldehydic group of **2c** and the active methylene group in **1a**.

We have also investigated the reaction of 2-thioxo-3-methyl-4-thiazolidinone (**1b**) with the same phosphonium ylides **2** to establish whether it would behave in a similar manner. We have found that the reaction product of *N*-methyl derivative **1b** with **2c**, in refluxing toluene, is assigned analogous structure **7b**, on the basis of IR, ^{1}H, ^{31}P, ^{13}C NMR, and mass spectral data (cf. Experimental).

The reaction of *N*-methyl derivative **1b** with ethoxycarbonylmethylenetriphenylphosphorane (**2a**) proceeds in refluxing toluene in the presence of triethylamine to give the olefinic product **8** in 90% yield along with triphenylphosphine sulfide (Scheme 2). The main features of the IR spectrum of **8** (in KBr) were the absence of the thiocarbonyl absorption band appearing in the spectrum of **1b** at 1175 cm^{-1} and the presence of absorption bands at 1710 (C=O, ester), 1680 (C=O, amide) and at 1623 cm^{-1} assigned for the olefinic stretching band. Moreover, the structure of the olefinic compound **8** is indicated by its analysis, ^{1}H, ^{13}C NMR, and mass spectral data (cf. Experimental).

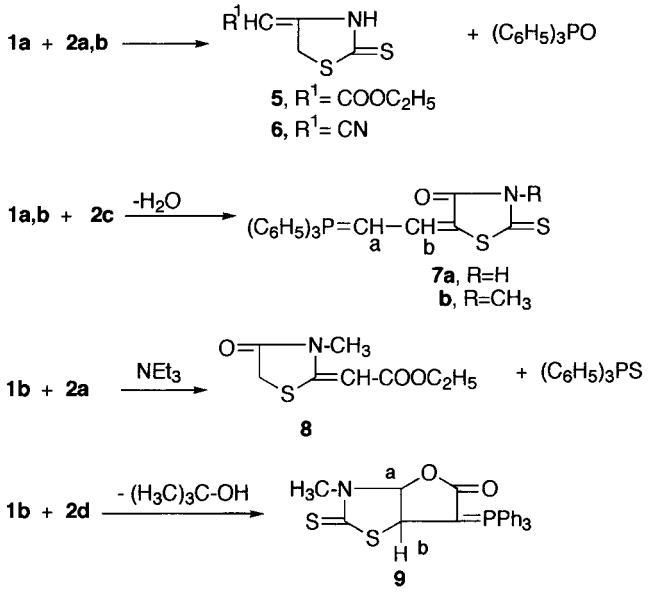
We have found that 2-thioxo-3-methyl-4-thiazolidinone (**1b**) reacts with an equimolar amount of tert-butoxycarbonylmethylenetriphenylphosphorane (**2d**) to give compound **9** in 65% yield (Scheme 2). Structure elucidation of product **9** has been determined on the basis of IR, ^{1}H, ^{13}C NMR, MS, and elemental analyses (cf. Experimental).

A possible explanation for the formation of product **9** is illustrated in Scheme 2. It may be considered that the lactone ylide **9** is formed by the lactonization of the dipolar ion via the extrusion of alcohol. Such an observation has been made before by Strandmann et al. [12].

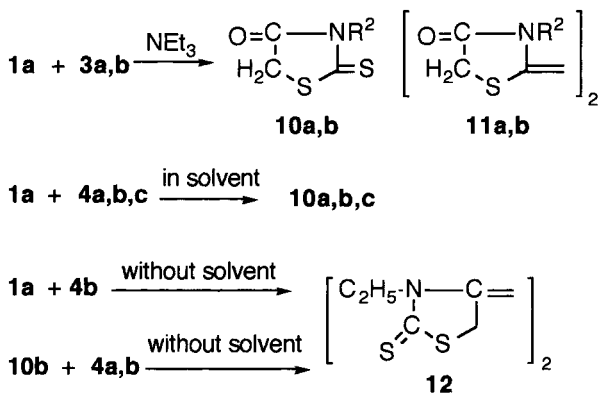
It can be concluded that the reaction of the 2-thioxo-4-thiazolidinone (**1a,b**) with Wittig reagents lead to different products, depending on the nature of the phosphorus ylide used as well as on the stability of the addition products [13].

Moreover, the reaction of **1a,b** with **2c** represents a novel method for the preparation of new complicated phosphonium ylides **7** via a simple method.

Furthermore, this study has been extended to include the reaction of **1a** with alkyl phosphites to examine whether the *S*-alkyl and the *N*-alkyl derivatives could be preferentially formed. When **1a** is allowed to react with freshly distilled dimethyl phosphite (**3a**), in 1 : 2 molar ratio in boiling toluene and in the presence of triethylamine, the known *N*-methyl-2-thioxo-4-thiazolidinone [14] (**10a**) and the compound **11a** are isolated (cf. Experimental, Scheme 3).



SCHEME 2



SCHEME 3

The IR spectrum of **11a** reveals the absence of C=S and NH absorption bands recorded at 1175 and 3235 cm^{-1}, respectively, in the starting thiazolidinone **1a**. The ^{13}C NMR of compound **11a** lacks the C=S signal recorded in compound **1a** at δ = 195.7.

Similarly, the reaction of **1a** with diethyl phosphite (**3b**) proceeds in boiling toluene and in the presence of triethylamine, to give the known [15] 2-thioxo-3-ethyl-4-thiazolidinone (**10b**) in 35% yield and the compound **11b** in 45% yield (cf. Experimental). The structure elucidation for compound **11b** is deduced from its elemental analysis, ^{1}H, ^{13}C NMR, and mass spectral data (cf. Experimental).

It is worth mentioning that compounds **10** and **11** are also formed when the reaction of rhodanine (**1a**) and dialkyl phosphites **3a,b** is conducted without solvents. Products **11a,b** are presumably formed via desulfurization of compound **10** (due to the presence of excess dialkyl phosphite).

The reaction of **1a** with trialkyl phosphites **4a–c** has also been investigated. When **1a** is allowed to react with one equivalent of trialkyl phosphites **4a–c**, in boiling benzene, the alkylated compounds **10a–c** are also obtained in good yield. The structures of compounds **10a–b** are deduced from comparative IR, ^{1}H NMR, and mass spectral data with authentic samples (cf. Experimental) [14,15].

The IR spectrum of **10c** lacks the NH absorption band appearing in the spectrum of **1a** at 3235 cm^{-1}.

When **1a** is allowed to react with triethyl phosphite **4c**, in absence of solvent at 70°C for 2 hours, compound **12** is isolated in 80% yield (Scheme 3). The structure of compound **12** is deduced from its analysis, IR, ^{1}H, ^{13}C NMR, and mass spectral data. The IR spectrum of product **12** lacks both the carbonyl and amide absorption bands at 1680 and 3235 cm^{-1}. Moreover, the presence of two quartets in the ^{1}H NMR spectrum of compound **12** suggests both the *Z* and *E* isomeric forms in equal percentage.

It is worth mentioning that when *N*-ethyl derivative **10b** is allowed to react with excess trimethyl and triethyl phosphites, without solvent at 80°C, the same compound **12** is isolated in 90% yield (cf. Experimental).

The results obtained in the present study have shown that alkyl phosphites can alkylate compounds of type **1a** to give the corresponding *N*-alkyl and not the *S*-alkyl derivatives. Moreover, the alkylating power of the phosphorus compounds studied increases in the order $(R^2O)_2P\text{-}OH < (R^2O)_3P$. The fact that dialkyl phosphites (DAP) are intermediate in alkylating power might be explained in terms of the presence of these compounds as tautomeric mixtures [16] of the trivalent and pentavalent states.

Experimental

All melting points are uncorrected. Benzene (thiophene free), toluene, and petroleum ether (boiling range, 60–80°C) were dried over sodium. Carbethoxymethylene-, cyanomethylene-, formylmethylene- and tert-butoxycarbonylmethylenetriphenylphosphoranes were prepared according to established procedures [17–19]. Dialkyl, trialkyl phosphites were prepared according to established procedures and were purified by fractional distillation [20–23]. The IR spectra were measured in KBr with a Perkin-Elmer infracord Spectrophotometer (model 157, Grating). The ^{1}H NMR spectra were recorded in $CDCl_3$ with JNM-GX-400 Spectrometer, Jeol. The ^{31}P NMR spectra were recorded in $CDCl_3$ (vs. H_3PO_4 as external standard) with a JNM-PS-100 Spectrometer, Jeol. ^{13}C NMR spectra were taken in $CDCl_3$ with JNM-PS-100 and JNM-GX-400 Spectrometer, Jeol. The mass spectra were run at 70 eV with Kratos MS equipment and a Varian MAT 311 A Spectrometer.

Reaction of 2-Thioxo-4-thiazolidinone (**1a**) *with Carbethoxymethylene-triphenylphosphorane* (**2a**). A mixture of **1a** (0.13 g, 1.0 mmol), ylide **2a** (0.33 g, 1.0 mmol), and 30 mL of dry toluene was refluxed for 4 hours. The volatile materials were evaporated under reduced pressure, and the residual substance was chromatographed on a silica gel column using ethyl acetate/toluene (5:95) as eluent to give product **5** as colorless crystals, yield 60%, m.p. 122–123°C. Anal. calcd for $C_7H_9NO_2S_2$ (203.27): C, 41.36; H, 4.46; N, 6.90; S, 31.55. Found: C, 41.30; H, 4.50; N, 6.80; S, 31.48%. MS, m/z (%): 203 (100) [M^+] using CI mode. IR: at 3235 cm^{-1} (NH), 1710 (C=O, ester), and 1622 cm^{-1} (C=C, olefinic). ^{1}H NMR: signals at δ = 1.34 (t, 3H, J_{HH} = 6 Hz, CH_3), 4.23 (q, 2H, J_{HH} = 6 Hz, CH_2), 3.51 (s, 2H, CH_2), 6.43 (s, 1H, =CH), and at δ = 11.52 (s, 1H, NH, exchangeable with D_2O). ^{13}C NMR: signals at δ = 167.6 (C=O, ester), 189.8 (C=S), 61.5 ($O\underline{C}H_2CH_3$), 32.9 ($\underline{C}H_2$), 13.2 ($OCH_2\underline{C}H_3$), and at δ = 133.2, 117.3 ($\underline{C}$=CH). Triphenylphosphine oxide was also isolated and identified.

Similarly, **1a** reacts with **2b** in dry toluene and was refluxed for 5 hours. The use of eluent acetone/petroleum ether (15:85) gave compound **6** as crystals, yield 90%, m.p. 171–172°C. Anal. calcd for $C_5H_4N_2S_2$ (156.23): C, 38.44; H, 2.59; N, 17.93; S, 41.05. Found: C, 38.40; H, 2.63; N, 17.88; S 41.10%. MS, m/z (%): 156 (100) [M^+]. IR: 3095 cm^{-1} (NH), 2884 (CN) and 1596 cm^{-1} (C=C, olefinic). ^{1}H NMR: δ = 3.91 (s, 2H, CH_2), 6.82 (s, 1H, =CH), 13.50 (s, 1H, NH, exchangeable with D_2O). ^{13}C NMR: δ =

190.3 (C=S), 107.9 (=CH-CN), 117.3 (=CHCN), and 32.2 (CH_2). Triphenylphosphine oxide was also isolated and identified.

Reaction of 2-Thioxo-4-thiazolidinone (**1a**) *with Formylmethylenetriphenylphosphorane* (**2c**). A mixture of **1a** (0.13 g, 1.0 mmol), ylide **2c** (0.30 g, 1.0 mmol), and dry toluene was refluxed for 8 hours. The volatile materials were evaporated in vacuo, and the residual substance was chromatographed on a silica gel column using eluent: methanol/chloroform (2:98) to give adduct **7a** as yellow crystals, yield 70%, m.p. 208–209°C. Anal. calcd for $C_{23}H_{18}NOPS_2$ (419.51): C, 65.85; H, 4.33; N, 3.34; P, 7.38; S, 15.29. Found: C, 65.80; H, 4.36; N, 3.30; P, 7.30; S, 15.20%. MS, m/z (%): 419 (95) [M^+]. IR: v = 3225 (NH), 1175 (C=S), 1700 (C=O), 1680, 1510 (C=P), 1430, 990 cm^{-1} (P–C, Phenyl) [24]. ^{1}H NMR: δ = 7.22 (dd, $^2J_{HP}$ = 18 Hz, J_{HH} = 6 Hz, H-a), 7.51 (dd, $^3J_{HP}$ = 10.5 Hz, J_{HH} = 6 Hz, H-b), 7.33–7.82 (m, 15H, aromatic), and at δ = 8.75 (s, NH, exchangeable with D_2O). ^{13}C NMR: signals at δ = 195.6 (C=S), 169.6 (C=O, thiazolidinone), 139.4 (d, $^2J_{CP}$ = 28 Hz, C^bH=C), 148.3 (d, $^3J_{CP}$ = 7.5 Hz, =C), 137.3 (d, $^1J_{CP}$ = 133 Hz, P=C) [25]. ^{31}P NMR: δ = +16.0.

Similarly, **1b** (0.14 g, 1.0 mmol) was reacted with ylide **2c** (0.30 g, 1.0 mmol) in 30 mL of dry toluene to give compound **7b** as a reddish yellow solid (eluent: chloroform/methanol, 95:05), yield 75%, m.p. 161–162°C. Anal. calcd for $C_{24}H_{20}NOPS_2$ (433.53): C, 66.50; H, 4.65; N, 3.23; P, 7.14; S, 14.80. Found: C, 66.45; H, 4.60; N, 3.20; P, 7.10; S, 14.75%. MS, m/z (%): 433 (100) [M^+]. IR: 1175 cm^{-1} (C=S), 1700 (C=O), 1685, 1515 (C=P), and 1435, 995 cm^{-1} (P-C, phenyl). ^{1}H NMR: δ = 3.43 (s, 3H, N–CH_3), 7.12 (dd, J_{HP} = 18 Hz, J_{HH} = 6 Hz, 1H, H-a), 7.61 (dd, $^3J_{HP}$ = 10.5 Hz, J_{HH} = 6 Hz, 1H, H-b), 7.31–7.82 (m, 15H, aromatic). ^{13}C NMR: δ = 31.2 (s, N–CH_3), 136.0 (d, $^1J_{CP}$ = 133 Hz, P=C), 169.0 (C=O, thiazolidinone), 198.0 (C=S), 139.2 (d, $^2J_{CP}$ = 28 Hz, C^bH=C), and 148.0 (d, $^3J_{CP}$ = 7.5 Hz, =C). ^{31}P NMR: δ = +16.0

Reaction of Carbethoxymethylenetriphenylphosphorane (**2a**) *with 2-Thioxo-3-methyl-4-thiazolidinone* (**1b**). A mixture of **2a** (0.34 g, 1.0 mmol), **1b** (0.14 g, 1.0 mmol), 30 mL of dry toluene and a few drops of triethylamine was refluxed for 4 hours. After evaporation of the volatile material under reduced pressure, the residue was subjected to silica gel column chromatography by using the eluent acetone/petroleum ether (30:70) to yield adduct **8** as colorless crystals, yield 90%, m.p. 88–89°C. Anal. calcd for $C_8H_{11}NO_3S$ (201.24): C, 47.75; H, 5.51; N, 6.96; S, 15.93. Found: C, 47.70; H, 5.56; N, 6.90; S, 15.90%. MS, m/z (%) = 201 (100) [M^+]. ^{1}H NMR: δ = 1.25 (t, J_{HH} = 6 Hz, 3H, C-CH_3), 4.25 (q, J_{HH} = 6 Hz, 2H, OCH_2), 3.62 (s, 2H, CH_2), 3.71 (s, 3H, N–CH_3), 6.52 (s, 1H, =CH). ^{13}C NMR: δ = 166.3 (C=O, ester), 169.9 (C=O, amide), 14.1 (C-CH_3), 62.03 (OCH_2), 34.5 (CH_2), 109.2 (=CH), 35.2 (N–CH_3), 86 (C=CH). Triphenylphosphine sulfide was also isolated from the reaction mixture and identified.

Reaction of Tert-butoxycarbonylmethylenetriphenylphosphorane (**2d**) *with 2-Thioxo-3-methyl-4-thiazolidinone* (**1b**). A mixture of **2d** (0.37 g, 1.0 mmol) and **1b** (0.14 g, 1.0 mmol) in 30 mL of dry toluene was refluxed for 6 hours. The volatile material was evaporated under reduced pressure and the residue subjected to silica gel column chromatography, the eluent being ethyl acetate/petroleum ether (95:05); **9** was obtained as yellow crystals from ethyl acetate, yield 65%, m.p. 263–264°C. Anal. calcd for $C_{24}H_{20}NO_2PS_2$ (499.53): C, 64.13; H, 4.48; N, 3.12; P, 6.89; S, 14.26. Found C, 64.10; H, 4.53; N, 3.6; P, 6.82; S, 14.20%. MS, m/z (%): 449 (90) [M^+]. IR: 1665 (C=O, pyrone), 1175 (C=S), 1670, 1510 (C=P), 1430, 995 cm^{-1} (P-C, phenyl). ^{1}H NMR: δ = 3.32 (s, N-CH_3), 5.01 (dd, $^3J_{HP}$ = 10 Hz, J_{HH} = 6.5 Hz, H-a), 5.05 (d, J_{HH} = 6.5 Hz, 1H, H-b), and at δ = 7.52–7.89 (m, 15H, aromatic). ^{13}C NMR: δ = 194.3 (C=S), 170.5 (d, C=O, $^2J_{PC}$ = 19 Hz), 30.4 (N–CH_3), 65.3 (C^a-H), 59.4 (d, C^b-H, $^2J_{PC}$ = 23 Hz), 134.6 (d, P=C, $^1J_{CP}$ = 130 Hz). ^{31}P NMR: δ = 18.7.

Reaction of 2-Thioxo-4-thiazolidinone (**1a**) *with Dimethyl Phosphite* **3a**. To a suspension of **1a** (0.13 g, 1.0 mmol) in dry benzene was added dimethyl phosphite (0.15 g, 2.0 mmol) and a few drops of triethylamine, and the reaction mixture was refluxed for 4 hours. The volatile material was evaporated under reduced pressure and the residue subjected to silica gel column chromatography; by use of the eluent acetone/petroleum ether (2:98), 3-methyl-2-thioxo-4-thiazolidinone (**10a**) was obtained as crystals, m.p. 67°C (mixed m.p. and comparative IR, ^{1}H-NMR, MS with authentic sample) [14].

11a (eluent 20:80) was obtained as orange crystals, yield 35%, m.p. 210–211°C. Anal. calcd for $C_8H_{10}N_2O_2S_2$ (230.31): C, 41.72; H, 4.38; N, 12.16; S, 27.84. Found: C, 41.69; H, 4.42; N, 12.12; S, 27.80%. MS, m/z(%): 230 (25) [M^+], 115 (100) [M^+-115). IR: 1680 cm^{-1} (C=O, amide), 1625 (C=C). ^{1}H NMR: δ = 3.45 [s, 6H, 2(N-CH_3)] and 3.89 [s, 4H, 2(CH_2)]. ^{13}C NMR: δ = 167.5 (C=O, thiazolidinone), 152.5 (C=C), 39.8 (CH_2), 38.2 (N-CH_3).

Similarly, thiazolidinone **1a** (0.13 g, 1.0 mmol) was reacted with diethyl phosphite **3b** (0.18, 2.0 mmol) in 30 mL dry toluene to give 3-ethyl-2-thioxo-4-thiazolidinone (**10b**) [eluent: ethyl acetate/petro-

leum ether (2:98), yield 35%, m.p. 38°C] (mixed m.p, comparative IR, 1H NMR, MS spectra with authentic sample) [15].

11b: Eluent (15:85), as yellowish green crystals, yield 45%, m.p. 228°C. Anal. calcd for $C_{10}H_{14}N_2O_2S_2$ (258.36): C, 46.49; H, 5.46; N, 10.84; S, 24.82. Found: C, 46.45; H, 5.43; N, 10.82; S, 24.80%. MS, m/z (%): 258 (25) [M^+], 179 (100) [M^+-179). IR: 1685 cm^{-1} (C=O, amide), 1625 (C=C). ^{1}H NMR: δ = 1.29 [t, 6H, 2(N-CH_2CH_3)], 3.95 [q, 4H, 2(N-CH_2CH_3)], 3.8 [s, 4H, 2(CH_2)]. ^{13}C NMR: δ = 165.9 (C=O), 152.4 (C=C), 40.3 (CH_2), 39.01, 11.75 (N-CH_2-CH_3).

The same reaction of **1a** and dialkyl phosphites **3a,b** was carried out without solvent to give adducts **11a** (yield 80%) and **11b** (yield 70%).

Reaction of 2-Thioxo-4-thiazolidinone (**1a**) *with Trialkyl Phosphites in the Presence of Solvent: General Method.* Starting material **1a** (1.0 mmol), alkyl phosphites **4a–c** (1.0 mmol) in dry benzene, and each reaction mixture was refluxed for 4 hours. The volatile materials were evaporated under reduced pressure, and the residue was subjected to silica gel column chromatography by using the eluent stated.

10a. Eluent: acetone/petroleum ether (2:98), m.p. 67°C [15].

10b. Eluent: ethyl acetate/petroleum ether (2:98), m.p. 38°C [16].

10c. Eluent: ethyl acetate/petroleum ether (5:95), m.p. 61–62°C, yield (70%).

IR: 1680 cm^{-1} (C=O, amide), 1175 cm^{-1} (C=S). ^{1}H NMR: δ = 1.40 [d, 6H, $CH(CH_3)_2$], 3.80 (s, 2H, CH_2), 5.15 (septet, 1H, CH, J_{HH} = 6 Hz).

Reaction of 2-Thioxo-4-thiazolidinone (**1a**) *with Triethyl Phosphite* **4b** *in Absence of Solvent.* A mixture of thiazolidinone **1a** (0.13 g) and 10 mL of triethyl phosphite **4b** was refluxed at 70°C. After evaporation of the volatile materials under reduced pressure, the residue was chromatographed on a silica gel column using acetone/petroleum ether (25:75) as eluent to give compound **12** as greenish yellow crystals, yield 60%, m.p. 179°C. Anal. calcd for $C_{10}H_{14}N_2S_4$ (290.49): C, 41.36; H, 4.86; N, 9.64; S, 44.15. Found: C, 41.33; H, 4.84; N, 9.63; S, 44.15%. MS, m/z (%): 290 (90) [M^+]. IR: 1175 cm^{-1} (C=S). ^{1}H NMR: δ = 1.34 [t, 6H, 2(N-CH_2CH_3)], 3.82 [s, 4H, 2(CH_2)], 3.95 (q, 2H, N-CH_2CH_3), 4.1 (q, 2H, N-CH_2CH_3).

Reaction of 3-Ethyl-2-thioxo-4-thiazolidinone (**10b**) *with Trimethyl Phosphite* **4a** *in Absence of Solvent.* A mixture of **10b** (0.16 g) and 10 mL of trimethyl phosphite **4a** was refluxed at 80°C for 3 hours. The volatile material was evaporated under reduced pressure and the residue subjected to silica gel column chromatography, eluent acetone/petroleum ether (25:75), to give compound **12** as greenish yellow crystals, yield 90% (m.p. and mixed m.p. 179°C). MS, m/z (%): 290 (100) [M^+]. ^{1}H NMR: δ = 1.34 [t, 6H, 2(N-CH_2-CH_3)], 3.82 [s, 4H, 2(C-CH_2)], 3.95 (q, 2H, N-CH_2-CH_3), 4.12 (q, 2H, N-CH_2-CH_3). ^{13}C NMR: δ = 195.5 (C=S), 148.6 (C=C), 38.4 (N-CH_2), 11.73 (N-CH_2-CH_3).

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