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Reaction of 5-Arylmethylene-2-thioxo-4-thiazolidinones with some Phosphonium Ylides. Synthesis of Thiazolidino[4,5-*x*]-Fused Compounds

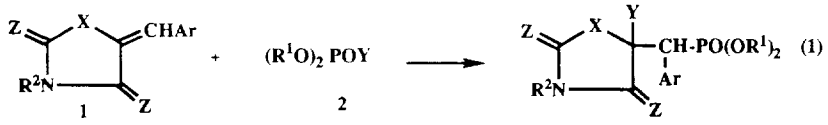
Wafaa M. Abdou,* El-Sayed M. A. Yakout and Neven A. F. Ganoub

National Research Centre, Dokki, Cairo, Egypt.

Abstract: The reactions of the entitled compounds (**4a**) and (**4b**) with some phosphonium ylides (**5a-d**) have been studied in considerable detail. By applying the Wittig reagents (**5a,b**) on the thiazolidinones (**4a,b**) in refluxing ethyl acetate and in the presence of triethylamine, conjugated dihydro-furo[2,3-*d*]thiazol-2(*3H*)-ones (**7a-d**) were obtained while carrying out the reaction in refluxing toluene and also in the presence of triethylamine led to the formation of the pyrone derivatives (**8**). Reaction of **4a,b** with oxoylide (**5c**), afforded the pyranderivatives (**10**). On the contrary, the reaction of **4a,b** with **5d** underwent 1,2-addition reaction to yield the new ylides (**12a,b**) as a sole reaction product. Except the last reaction of **4a,b** with **5d**, other reactions afforded, in each instance, the olefinated products (**9a-d**) and (**11a,b**) in 11-18% yield.

INTRODUCTION

Thiazolidinones which belong to an important group of heterocyclic compounds have been subject of extensive study in the recent past. Numerous reports have appeared which highlight their chemistry and use.[1-3] Diverse biological activities such as bactericidal, pesticidal, fungicidal, insecticidal, anticonvulsant, tuberculostatic, antiinflammatory, antithyroidal, potentiation of pentobarbital-induced sleeping time, etc., have been found to be associated with thiazolidinone derivatives.[3,4] In recent years, therefore, several new methods for the preparation of thiazolidinone derivatives and reactions have been reported in the literature.[5-7] However, little attention has been directed to the behaviour of this class of compounds toward phosphorus reagents. As early as 1976 and 1978, it was reported that phosphite esters attack 2- and 4-thiazolidinones (**1**), preferably, at the exocyclic ethylene bond by 1,2-addition to give phosphorylated compounds (**3**) as a sole reaction product



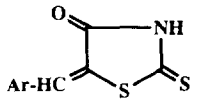
1 2 3

X = S, SO_2, Z = O, S
R^2 = H, alkyl, aryl

R^1 = alkyl
Y = H, R^1

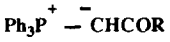
* To receive any correspondence.

(eq. 1).[8,9] Our continuous interest in the preparation and study of reactions of thiols and thiazoles with phosphorus reagents[10-14] prompted us to examine the behaviour of 5-arylmethylene-2-thioxo-4-thiazolidinones (also known as 5-arylidenerhodanines)[4] **(4a)** and **(4b)** toward some phosphonium ylides **(5a-d)** under varied conditions to determine whether their reaction differed from those of the phosphorus reagents **(2)**.[8,9] This had been done and indeed, significant deviation from usual behaviour have been noted



4

a, Ar = C_6H_5
b, Ar = C_6H_4-OH-o



5

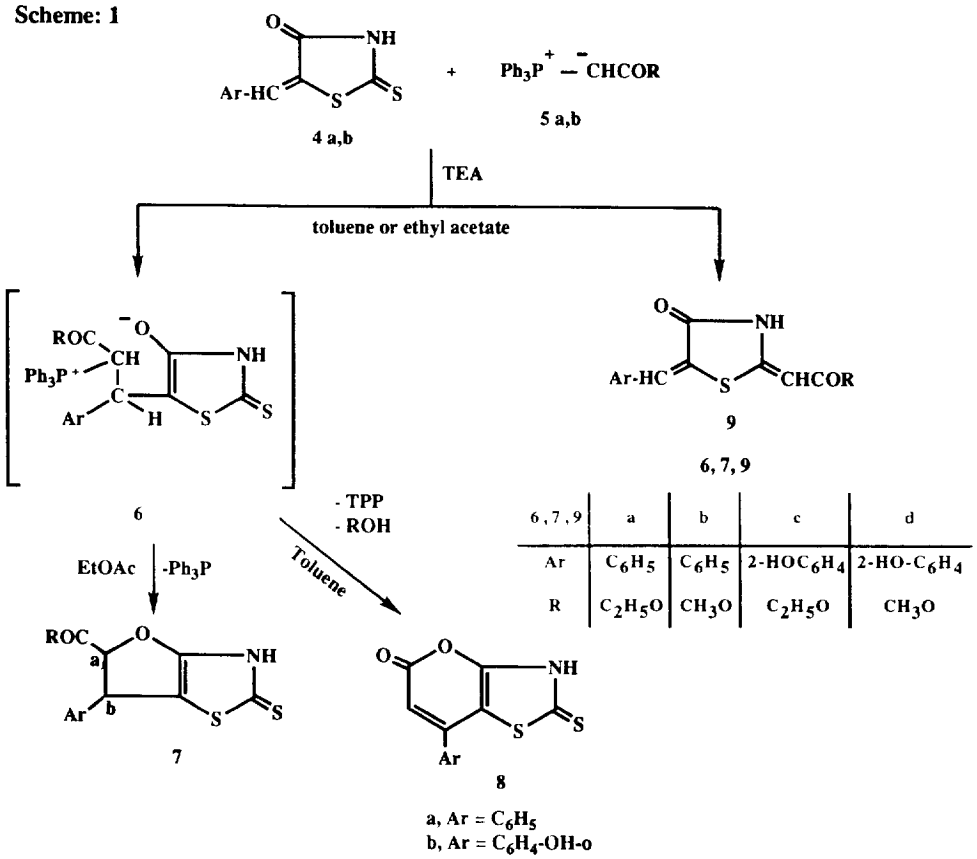
a, R = OC_2H_5
b, R = OCH_3
c, R = CH_3
d, R = H

RESULTS AND DISCUSSION

5-Benzylidenerhodanine **(4a)** on treatment with ethoxycarbonylmethylenetriphenylphosphorane **(5a)** in boiling tetrahydrofuran, the educts remained practically unchanged, even after 18 h. On the other hand, the reaction was completed when it was carried out in refluxing ethyl acetate and in the presence of triethylamine. Chromatographic separation produced successively four different substances. The first two of which were proved to be, respectively, triphenylphosphine and triphenylphosphine sulfide. The third product **9a** was obtained in ~18% yield as yellow crystals and deduced to have diolefinic structure from its analysis and spectral data. The IR spectrum (KBr, expressed in cm^{-1}) of **9a** exhibits strong absorption bands at 3235 (NH), 1710 (C=O, ester), 1680 (C=O, amide) and at 1622, 1606 assigned for the two olefinic stretching bands. Moreover, the IR spectrum lacks the thiocarbonyl absorption band appearing in the spectrum of **4a,b** at 1175 cm^{-1}. The ^{1}H-NMR spectrum of compound **9a** exhibits signals at δ 1.23 (t, 3H, C-CH_3, J_{HH} = 6 Hz) and 3.58 (q, 2H, CH_2, J_{HH} = 6 Hz). The two olefinic protons and the five aromatic protons appeared as a complex pattern in the 7.3-7.75 ppm region. Its ^{13}C-NMR spectrum also supported the proposed structure (see experimental). Thus, for example, it showed signals at δ_C 169.4 (C=O, thiazolidinone) and 166.7 (C=O, ester). The mass spectrum of **9a** showed the ion peak at m/z = 275 [M^+]. The last isolated substance was substituted dihydrofuro[2,3-*d*] thiazol-2(3*H*)-one **(7a)** in ~46% yield as evidenced by elemental analysis, IR, NMR and mass spectral data. Its IR spectrum showed the absence of absorption bands at 1680 and 1622 cm^{-1} attributed to C=O and C=CH bands of compound **4**. It showed bands at 3220 (NH), 1714 (C=O, ester), 1097 (dihydrofuran) and 1175 cm^{-1} (C=S). The ^{1}H-NMR spectrum of **7a** had signals at δ 1.25 (t, 3H, C.CH_3), 3.55 (q, 2H, OCH_2), 7.15-7.72 (m, 5H, Ar-**H**) and at 8.5 ppm (br., 1H, NH). Protons of the dihydrofuran nucleus appeared as two doublets 3.2 (d, 1H, O-**CH**a, J_{HH} = 6.5 Hz) and 3.8 ppm (d, 1H, **CH**b, J_{HH} = 6.5 Hz). The ^{13}C-NMR showed signals at δ = 195.7 (**C**=S); 164.99 (C=O); 31.5, 27.5 (HC-**CH**); 15.2, 58.9 (OEt). Moreover, the mass spectrum of **7a** showed the ion peak at m/z = 307 [M^+]. These data can be readily interpreted in terms of structure **7**.

On the other hand, it was found that when the above reaction **(4a + 5a)** was allowed to proceed in refluxing toluene instead of ethyl acetate, and in the presence of triethylamine, the reaction required much longer time to be completed, yielding a yellow substance in ~52% yield which was proved to be a fused pyrano-thiazolone **8a** and besides this **9a** as a byproduct in ~11% yield was obtained. Triphenylphosphine and triphenylphosphine sulfide were also isolated from the product mixture. However, the deviation of the reaction

Scheme: 1



6,7,9	a	b	c	d
Ar	C_6H_5	C_6H_5	2-HOC_6H_4	2-HO-C_6H_4
R	C_2H_5O	CH_3O	C_2H_5O	CH_3O

course in toluene from what precedently has been found in ethyl acetate can be reasonably interpreted in the light of the reaction conditions such as the polarity and the temperature.

The coumarin structure **8a** has been elucidated as follows: (a) Its IR spectrum revealed the absence of C=O and C=CH absorption bands recorded for **4a** at 1680 and 1622 cm^{-1}, respectively. The spectrum showed, however, strong absorption bands at 3235 (NH), 1665 (C=O, pyrone), 1175 (C=S) and at 1065 cm^{-1} (C=C-O). (b) The ^{1}H-NMR spectrum of **8a** in $CDCl_3$ showed only a multiplet in the region δ 7.3-7.78 due to the aromatic protons and a broad signal (exchangeable with D_2O) at 8.75 ppm attributed to the NH group. (c) Its ^{13}C-NMR showed signals at δ = 195.5 (**C**=S); 159.5 (**C**=O); 148.3, 142.4 (**C**=**C**). (d) The mass spectrum of **8a** displayed a molecular ion peak at m/z = 261 [M^+].

Obviously, the dipolar intermediate **6** formed from the initial attack of the carbanion centre in the Wittig reagent **5** on the active exocyclic electrophilic carbon atom of the ∝, β-unsaturated system in **4**, undergoes O-alkylation with triphenylphosphine elimination to give the conjugated dihydro-furo[2,3-*d*] thiazol-2(3*H*)-ones **7**.[15,16] On the other hand, formation of **8** can be explained via an internal Hofmann elimination of triphenylphosphine from the betaine **6** accompanied by spontaneous δ-lactonization[17]via the extrusion of a suitable moiety (i.e., RH, R = OC_2H_5). However, the formation of the olefinic product (**9**) can be interpreted by the concurrent thiophilic attack on **4** by the nucleophile **5** to yield the Wittig-type-product (**9**) via the

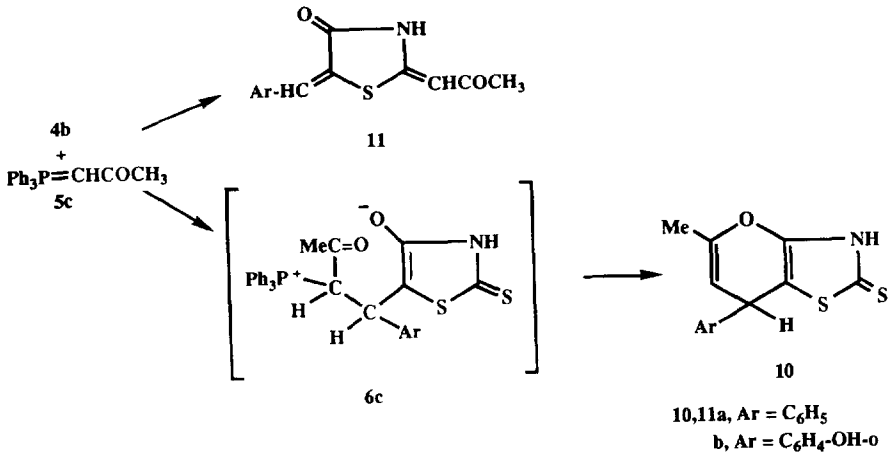
extrusion of triphenylphosphine sulfide (Scheme 1).

To demonstrate a general character of the synthesis of the fused dihydro-furo-thiazolones (**7**) and pyrano-thiazolones **8**, the reaction was performed with four different ylides (**5a-d**) shown above and two 5-substituted thiazolidinones (**4a**) and (**4b**) whereas **7b** and **8a** were obtained, respectively, when **4a** was allowed to react with methoxy- carbonylmethylenetriphenylphosphorane (**5b**) in refluxing ethyl acetate and refluxing toluene, and in the presence of triethylamine. The olefinic product (**9b**) was also obtained in both instances. Similarly, the reaction of o-hydroxybenzylidenerhodanine (**4b**) with **5a** or **5b** proceeds in refluxing ethyl acetate or toluene and in the presence of triethylamine to give the products **7c,d** and **9c,d** or **8b** and **9c,d**, respectively. Triphenylphosphine and triphenylphosphine sulfide were also isolated from the reactions. All the isolated products were identified by spectral methods (see expermintal). On the other hand, reactions of **4a,b** with phosphonium ylides (**5c**) or (**5d**) underwent different courses.

When compound **4a** or **4b** was treated with acetonylidenetriphenylphosphorane (**5c**) in refluxing ethyl acetate (or toluene) and in the presence of triethylamine, neither the substituted dihydro-furans (**7**) nor the coumarine (**8**) was formed. Instead of them, the substituted pyrans (**10a,b**) were obtained in ~55% yield together with a small amount ~12% yield of the olefin **11** which was identified by spectral methods (*cf.* experimental).

The pyran structure **10** was established by the following physical and spectral data: (a) Elemental analysis and molecular weight determination (MS) of **10a** support the molecular formula $C_{13}H_{11}NOS_2$ (261.37); accordingly, MS: m/z = 261 [M^+]. (b) It showed an infrared absorption bands at 3225 (NH), 1175 (C=S) and 1075 cm^{-1} (C=C-O). (c) The ^{1}H-NMR spectrum of **10a** exhibited signals at δ 1.85 (s, 3H, CH_3), 4.1 (s, 1H), 7.3-7.8 ppm (m, 6H) and at 8.55 ppm (br. 1H). ^{13}C-NMR had signals at δ_C 195.78 (C=S); 27.9 (CHAr); 24.6 (CH_3).

Scheme: 2

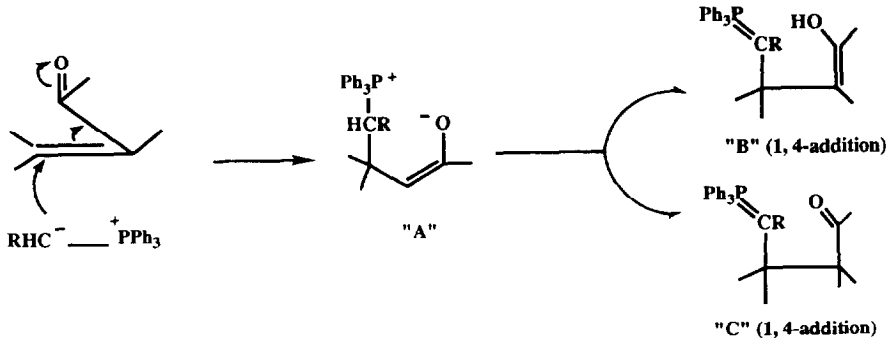


It is reasonable to assume that the initial dipolar structure **6c**, formed from **4** and **5c** was converted by an internal Wittig reaction, invoked by the ß-oxophosphorus ylide (**5c**), to **10** (Scheme 2). A similar result was observed by Sorensen et al[18] and others. [19-21]

It should be noted that the presented behaviour of the Wittig reagents (**5a-c**) toward thiazolidinones (**4a**) and (**4b**) is in marked disparity with the behaviour of the same reagents toward many other ∝,β unsaturated

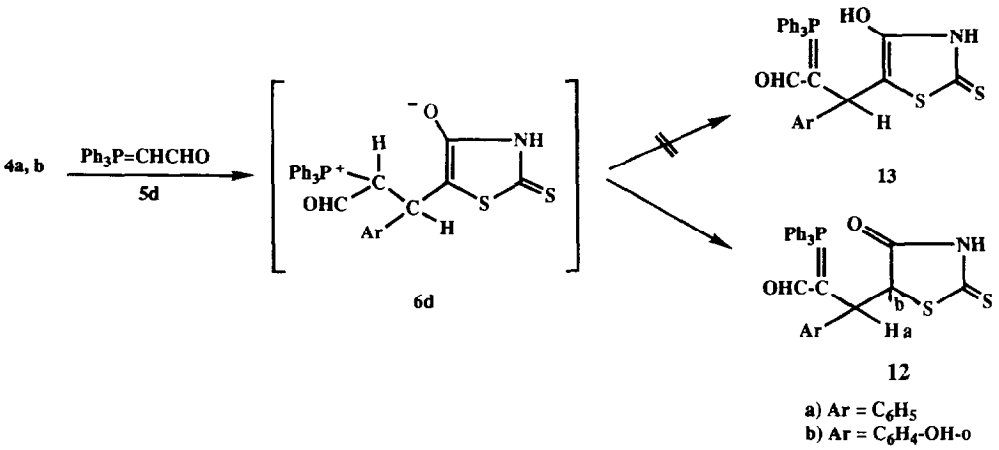
systems. In the latter case, the phosphonium intermediate "**A**" (Scheme 3), initially formed, is either resonance-stabilizd or undergoes ∝-proton migration to the electron rich centre (Hofmann transylidation) of the molecule to give, finally, a new stable-ylide *via* 1,4-"**B**" or 1,2 addition "**C**".[19, 22-24]

Scheme: 3



Next, treatment of **4a,b** with formylmethylenetriphenylphosphorane (**5d**) in refluxing toluene (or ethyl acetate) and in the presence of triethylamine, led to the formation of the new complex phosphonium ylides **12a,b** as a sole reaction product. Structure **12** was in accord with the elemental and spectral data, ^{31}P-NMR spectrum of **12a** exhibits a positive shift at δ 22.4 ppm, *vs.* H_3PO_4).The ^{13}C-NMR spectrum of **12a** showed signals at δ 205.3 (CHO), 195.76 (C=S), 169.4 (C=O), 151.4 (C=P, J_{cp} = 147 Hz). Its ^{1}H-NMR spectrum of signals at δ = 3.3 (d of d, $^3J_{HP}$ = 10.5 Hz) and at δ 4.1 (d, J_{HH} = 6.5 Hz) corresponding to the methine protons (a) and (b), respectively. However, the presence of the AB system (CH-CH) and the lack of a signal due to a

Scheme: 4



hydroxyl group in ^{1}H-NMR spectrum of **12a**; as well as the persistence of the thiazolidinone-carbonyl band in its IR and ^{13}C-NMR spectra, confirm the assigned structure **12** and rule out other alternative, its tautomer, structure **13**. Michael addition of the ylide species **5d** to the active methine carbon in compound **4** affords the phenoxy anion intermediate (**6d**). Transfer of a proton from ∝- to the γ- carbon atom leads to the new phosphorane **12**.[23,24]

In summary, in this paper we reported a general synthesis of several new cyclic and acyclic derivatives of 4-thiazolidinones and presented a diverse reactivity of Wittig reagent toward ∝, β-unsaturated carbonyl compounds. Even though, the manuscript describes the competition between two options available to a stabilized ylide in the reaction with **4a** and **4b**, i.e. olefination or conjugate addition, it is obvious that the exocyclic ethylenic part of the ∝, β-unsaturated carbonyl system in **4** is the most vulnerable site of attack by the nucleophilic phosphorus reagents **5a-d**. This seems to be attributable partly to the activation of the olefinic bond by the electronegative carbonyl group; and partly to the deactivation of the thioxo-function by its thioamidic nature. Notably, this competition have not been observed when **4a,b** were allowed to react with phosphite esters (**2**) whereas, only, phosphorylated compounds (**3**) were obtained *via* 1,2-addition (see eq. 1).[8,9]

EXPERIMENTAL

Melting points are uncorrected. IR spectra were obtained with a Perkin Elmer Infracord Spectrometer Model 197 (Grating) in KBr. ^{1}H- and ^{13}C-NMR spectra were recorded with $CDCl_3$ or [D_6]DMSO as solvents with a Bruker Spectrometer Model WH-90 and the chemical shifts were recorded in δ ppm relative to TMS. The ^{31}P NMR spectra were taken with a Varian CFT-20 (*vs.*, external 85% H_3PO_4). The mass spectra were performed at 70 eV with MS-50 Kratos (A.E.I.) Spectrometer provided with a data system. Elemental analyses were carried out at the Microanalysis Laboratory, National Research Centre, Cairo.

Reaction of 5-Arylmethylene-2-thioxo-4-thiazolidinones (4a) and (4b) with Phosphorus Ylides (5a,b). A solution of **4a**[25] (2.2 g, 10 mmol) and ethoxycarbonylmethylenetriphenylphosphorane acetate (**5a**)[26] or methoxycarbonylmethylenetriphenylphosphorane (**5b**)[26] (15 mmol) in ethyl acetate (50 ml) containing triethylamine (0.5 ml) was refluxed for 24 h. After evaporation of the solvent, the remainder was subjected to column chromatography [silica gel, pet. ether/ acetone (9:1 v/v) with increasing amounts of acetone (up to 3:1)]. The first two products were triphenylphosphine and triphenylphosphine sulfide which were isolated and identified.

The fraction up to 7:3 v/v gave compounds **9a** or **9b**.

9a was obtained as yellow crystals (51 mg, 18.4%) m.p. 145-147 °C (hexane). IR (KBr): 3235, 1710, 1980, 1622, 1606 cm^{-1}. ^{1}H-NMR ($CDCl_3$) : δ = 1.23 (t, J_{HH} = 6 Hz, 3H), 3.58 (q, 2H, J_{HH} = 6 Hz), 7.3 - 7.75 (m, 7H), 8.3 ppm (br., 1H).^{13}C-NMR ($CDCl_3$): δ 169.4, 166.7 (**C**=O); 139.4, 131.6 (=**C**H); 13.8 (**C**H_3), 61.2 (O**C**H_2). MS : m/z (%) = 275 (22) [M^+].

$C_{14}H_{13}NO_3S$ (275.33) Calcd. C 61.07 H 4.76 N 5.08 S 11.65
Found: C 61.26 H 4.64 N 4.88 S 11.51.

9b was obtained as yellow crystals (41 mg, 15.8%) m.p. 152-154 °C (hexane). IR (KBr): 3260, 1719, 1685, 1637, 1610 cm^{-1}. ^{1}H-NMR ($CDCl_3$) : δ_c = 3.55 (s, 3H), 7.1 - 7.78 (m, 7H), 8.5 ppm (br., 1H). MS: m/z (%) = 261 (18) [M^+].

$C_{13}H_{11}NO_3S$ (261.31) Calcd. C 59.75 H 4.24 N 5.36 S 12.27
Found: C 59.92 H 4.09 N 5.1 S 12.16

The fraction up to 3:7 v/v yielded compound **7a** or **7b**.

7a was obtained as orange crystals (1.4 g, 45.7%) m.p. 225-227 °C (benzene). IR (KBr) : 3220, 1714, 1175, 1097 cm^{-1}. ^{1}H-NMR ($CDCl_3$) : δ = 1.25 (t, 2H, J_{HH} = 6 Hz), 3.2 (d, 1Ha, J_{HH} = 6.5 Hz), 3.55 (q, 2H, J_{HH} = 6 Hz), 3.8 (d, 1Hb, J_{HH} = 6.5 Hz), 7.15 - 7.72 (m, 5H), 8.5 ppm (br., 1H).^{13}C-NMR ($CDCl_3$): δ_c 195.7 (**C**=S); 164.99 (**C**=O) ester); 145.7, 141.5 (**C**=**C**); 31.5, 27.5 (**C**H=**C**H); 15.2, 58.9 (OEt). MS: m/z

(%) = 307 (33) [M^+].

$C_{14}H_{13}NO_3S_2$(307.4) Calcd. C 54.7 H 4.26 N 4.55 S 20.86
Found: C 54.91 H 4.34 N 4.28 S 20.67.

7b was obtained as orange crystals (1.4 g, 48.5%) m.p. 228 - 230 °C (benzene). IR (KBr): 3235, 1720, 1185, 1090 cm^{-1}. ^{1}H-NMR ($CDCl_3$) : δ = 4.1 (d, 1Ha, J_{HH} = 7 Hz), 4.2 (s, 3H), 4.35 (d, 1Hb, J_{HH} = 7 Hz), 7.3 - 8 (m, 5H), 8.5 ppm (br., 1H). MS : m/z (%) = 293 (20) [M^+].

$C_{13}H_{11}NO_3S_2$(293.37) Calcd. C 53.22 H 3.78 N 4.77 S 21.86
Found: C 53.45 H 3.62 N 4.55 S 21.93.

When the above reaction was repeated in boiling toluene and in the presence of triethylamine, compound **9a** or **9b** was isolated first in 11.8 and 10.4% yield, respectively, while the fraction up to 1:1 v/v yielded, in each instance, compound **8a** as yellow crystals in 52.4% yield, m.p. 184-185 °C (benzene). IR (KBr): 3235, 1665, 1175, 1065 cm^{-1}. ^{13}C-NMR ($CDCl_3$): δ 195.7 (**C**=S); 159.5 (**C**=O), 148.3, 142.4 (**C**=**C**). - MS: m/z (%) = 261 (30) [M^+].

$C_{12}H_7NO_2S_2$ (261.33) Calcd. C 55.15 H 2.7 N 5.36 S 24.55
Found: C 55.32 H 2.62 N 5.18 S 24.72.

Similarly, the products **9c,d** and **7c,d** were obtained upon reacting the thiazolidinone (**4b**)[25] (2.4 g, 0.01 mol) with alkoxycarbonylmethylenetriphenylphosphorane (**5a**) and (**5b**) (0.015 mol) in refluxing ethyl acetate containing triethylamine (0.5 ml) for 18 h and working up of the reaction mixture as mentioned above. Triphenylphosphine and triphenylphosphine sulfide were first isolated and identified.

9c was obtained as yellow crystals (41 mg, 14.3%), m.p. 120 - 122 °C (acetone). IR (KBr): 3550, 3225, 1720, 1622 cm^{-1}. ^{1}H-NMR ($CDCl_3$) : δ = 0.85 (t, 3H, J_{HH} = 6 Hz), 4.2 (q, 2H, J_{HH} = 6 Hz), 7.3 - 7.85 (m, 7H), 8.5 (br, 1H), 9.5 ppm (br, 1H). MS: m/z (%) = 291 (13) [M^+].

$C_{14}H_{13}NO_4S$ (291.323) Calcd. C 57.72 H 4.5 N 4.81 S 11.00
Found: C 57.86 H 4.45 N 4.72 S 10.73.

9d was obtained as yellow crystals (46 mg, 16.7%), m.p. 125 - 127 °C (acetonitrile). IR (KBr) : 3345, 3235, 1710, 1620 cm^{-1}. ^{1}H-NMR ($CDCl_3$) : δ = 3.83 (s, 3H), 7.1 - 7.82 (m, 7H), 8.7 (br 1H), 9.5 ppm (br, 1H). MS : m/z (%) = 277 (40) [M^+].

$C_{13}H_{11}NO_4S$ (277.3) Calcd. C 56.31 H 4.0 N 5.05 S 11.56
Found: C 56.46 H 3.87 N 4.85 S 11.43.

The fraction up to 3 : 7 v/v yielded compound **7c** or **7d**.

7c was obtained as orange crystals (1.8 g, 55.6%), m.p. 194 - 196 °C (benzene). IR (KBr) : 3355, 3220, 1720, 1180, 1090 cm^{-1}. ^{1}H-NMR ([d] DMSO) : δ = 1.15 (t, 3H, J_{HH} = 6 Hz), 3.05 (q, 2H, J_{HH} = 6 Hz), 3.15 (d, 1Ha, J_{HH} = 7 Hz), 3.35 (d, 1Hb, J_{HH} = 7 Hz), 7.45 - 7.78 (m, 5H), 8.5 (br., 1H), 9.5 ppm (br. 1H). ^{13}C-NMR ([d]DMSO): δ_C 195.5 (**C**=S); 165.3 (**C**=O), 145.2, 140.4 (**C**=**C**); 151.3 (**C**-OH); 15.3, 58.7 (OEt). MS : m/z (%) = 323 (25) [M^+].

$C_{14}H_{13}NO_4S_2$ (323.398) Calcd. C 51.99 H 4.05 N 4.33 S 19.83
Found: C 51.85 H 3.88 N 4.20 S 19.67.

7d was obtained as orange crystals (1.5 g, 48.2%), m.p. 205 - 207 °C (benzene). IR (KBr): 3345, 3230, 1710, 1175, 1085 cm^{-1}. ^{1}H-NMR ([d] DMSO) : δ = 4.1 (d, 1Ha, J_{HH} = 7 Hz), 4.2 (s, 3H), 4.3 (d, 1Hb, J_{HH} = 7 Hz), 7.35 - 7.88 (m, 5H), 8.2 (br., 1H), 9.5 ppm (br. 1H). MS: m/z (%) = 309 (22) [M^+].

$C_{13}H_{11}NO_4S_2$ (309.371) Calcd. C 50.47 H 3.58 N 4.53 S 20.73

Found: C 50.54 H 3.42 N 4.39 S 20.66.

When the same reaction was repeated in boiling toluene, compound **9c** or **9d** was firstly obtained in 12.5 and 14.7% yield, respectively. The fraction up to 1:1 v/v yielded, in each instance, compound **8b** as yellow crystals in ~ 58.4% yield, m.p. 168-170 °C (chloroform). IR (KBr): 3345, 3220, 1665 cm^{-1}. ^{13}C-NMR ($CDCl_3$): δ_C 195.7 (**C**=S); 159.5 (**C**=O); 151.4 (**C**-OH) 148.5, 141.9 (**C**=C). MS: m/z (%) = 277 (50) [M^+].

$C_{12}H_7NO_3S_2$ (277.328) Calcd. C 51.97 H 2.54 N 5.05 S 23.12
Found: C 52.22 H 2.37 N 4.86 S 23.01.

No reaction was observed, however, in a parallel experiment when the reactants (**4a,b + 5a,b**) were refluxed in tetrahydrofuran even after 18 h.

Reaction of (4a) and (4b) with (5c). To a solution of acetonylidenetriphenylphosphorane (**5c**)[27] (4.7 g, 0.015 mol) in 20 ml ethyl acetate (or toluene) was added a solution of thiazolidinone **4a** (2.2,g, 0.01 mol) or **4b** (2.3 g, 0.01 mol) in 30 ml of the same solvent and the reaction mixture was refluxed for 36 h in the presence of triethylamine (0.5 ml). The product mixture was worked up as above whereas triphenylphosphine sulfide and triphenylphosphine oxide were the first two products, respectively. Compound **11a** or **11b** was eluted thirdly.

11a was obtained as yellow crystals (33 mg, 13.5%), m.p. 118-120 °C (methylene chloride). IR (KBr): 3225, 1725, 1625 cm^{-1}. ^{1}H-NMR : δ = 2.05 (s, 3H), 7.1 - 8.0 (m, 7H), 8.7 (br., 1H). MS: m/z (%) = 245 (40) [M^+].

$C_{13}H_{11}NO_2S$ (245.305) Calcd. C 63.65 H 4.52 N 5.71 S 13.07
Found: C 63.77 H 4.46 N 5.53 S 12.86.

11b was obtained as yellow crystals (33 mg, 12%) m.p. 110-112 °C (acetonitrile). - MS: m/z (%) = 261 (50) [M^+].

$C_{13}H_{11}NO_3S$ (261.305) Calcd. C 59.75 H 4.24 N 5.36 S 12.27
Found: C 59.86 H 4.16 N 5.16 S 12.14

Elution with pet. ether - ethyl acetate (2 : 8 v/v) afforded compound **10a** or **10b**.

10a was obtained as yellow crystals (1.4 g, 55.2%) m.p. 165 - 167 °C (hexane) IR (KBr): 3225, 1175, 1075 cm^{-1}. ^{1}H-NMR ($CDCl_3$) : δ = 1.85 (s, 3H), 4.1 (s, 1H), 7.3 - 7.8 (m, 6H), 8.45 ppm (br. 1H). .^{13}C-NMR ($CDCl_3$): δ_C 195.78 (**C**=S), 27.9 (**C**HAr), 24.6 (CH_3) MS: m/z (%) = 261 (32) [M^+].

$C_{13}H_{11}NOS_2$ (261.371) Calcd. C 59.74 H 4.24 N 5.36 S 24.53
Found: C 59.48 H 4.17 N 5.25 S 24.39

10b was obtained as yellow crystals (1.5 g, 55.8%) m.p. 158-160 °C (hexane). ^{1}H-NMR ($CDCl_3$): δ = 1.87 (s, 3H), 4.16 (s, 1H), 7.3-7.78 (m, 5H), 8.44 (br. NH), 9.5 (OH). .^{13}C-NMR ($CDCl_3$): δ_C =195.74 (**C**=S), 151.8 (Ar-OH), 27.82 (**C**HAr), 24. 57 (CH_3). MS : m/z (%) = 277 (55) [M^+].

$C_{13}H_{11}NO_2S_2$ (277.37) Calcd. C 56.29 H 3.99 N 5.05 S 23.12
Found: C 56.43 H 3.87 N 4.84 S 22.98

Reaction of 4a and 4b with 5d : A mixture of **4a** or **4b** (0.01 mol) and formylmethylene-triphenylphosphorane (**5d**)[28] (4.5 g, 0.015 mol) in ethyl acetate (or toluene) (100 ml) containing triethylamine (0.5 ml) was refluxed for 30 h. After the volatile material were distilled under reduced pressure, the residue was treated with dry ether, filtered and crystallized from chloroform to give the new thiazolidinonephosphonium ylide derivative **12a** or **12b**, respectively, as yellow crystals.

Compound **12a** (3.8 g, 72.6%) m.p. 228-230 °C (benzene). IR (KBr): 3245, 1720, 1680, 1450, 1155 cm^{-1}. ^{1}H-NMR ($CDCl_3$) : δ = 3.3 (d of d, 1Ha, $^3J_{HP}$ = 10.5 Hz), 4.1 (d, 1Hb, J_{HH} = 6.5 Hz), 7.3 - 7.8 (m, 21 H), 7.98 ppm (br. 1H).^{13}C-NMR ($CDCl_3$): δ_C =195.76 (**C**=S), 169.4 (**C**=O), 151.4 (**C**=P, d, J_{cp} = 147.6 Hz), 33.6, 28.2 (CH-CH). ^{31}P-NMR ($CDCl_3$) : δ = 22.4 ppm. MS : m/z (%) = 525 (12) [M^+].

$C_{30}H_{24}NO_2PS_2$ (525.64) Calcd. C 68.55 H 4.6 N 2.66 P 5.89 S 12.2
Found: C 68.72 H 4.54 N 2.43 P 5.97 S 12.05

Compound **12b** (4 g, 75.4%) m.p. 218-220 °C (benzene). IR (KBr): 3340, 3255, 1710, 1680 cm^{-1}. ^{1}H-NMR ($CDCl_3$) : δ = 3.1 (d of d, 1Ha, $^3J_{HP}$ = 11.5 Hz), 4.25 (d, 1Hb, J_{HH} = 7 Hz), 7.3 - 7.8 (m, 20H), 8.6 (br., 1H), 9.5 ppm (br., 1H).^{13}P-NMR ($CDCl_3$): δ = 24.3 ppm. MS : m/z (%) = 541 (18) [M^+]

$C_{30}H_{24}NO_3PS_2$ (541.642) Calcd. C 66.52 H 4.46 N 2.58 P 5.72 S 11.84
Found: C 66.65 H 4.32 N 2.34 P 5.85 S 11.78

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