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# Selective Addition of Wittig Reagents to Bifunctionalized Compounds. Condensation of 3-Phenyl (2-benzothiazolyl)acrylonitrile with some Phosphorus Ylides

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**Abstract**: The behaviour of the acrylonitrile 1 toward different types of phosphorus ylides such as alkoxycarbonyl- **2a,b** and  $\beta$ -keto-alkylidene phosphoranes **2c-e** as well as arylidenephosphorane **3** has been studied. The reactions take different pathways leading to unusual products, depending only on the nature of the substituents of ylides used. All reactions proceed only in the presence of a base whereby a variety of 1,3-benzothiazolyl-[1,2-x] fused compounds, e.g. **6, 16** and **18**; cyclopropene- **15** and cyclopropane- **19** derivatives as well as different types of new ylides: **7, 10** and **12a,b** were isolated and established on chemical and physical evidence. © 1998 Published by Elsevier Science Ltd. All rights reserved.

## INTRODUCTION

In connection with other investigations,<sup>1-6</sup> we were interested in determining how well the reaction proceeds between  $\alpha$ , $\beta$ -unsaturated nitriles and the phosphorus ylides. With this aim, we studied the interaction of the crystalline 2-benzylidenecyanomethyl-1,3-benzothiazole 1 and three types of stabilized Wittig reagents: alkoxycarbonyl- **2a,b** and  $\beta$ -keto-methylenetriphenylphosphoranes **2c-e** as well as arylidene- phosphorane 3. The incentive in this direction is based upon recorded potencies of the thiazole nucleus<sup>7,8</sup> and of the unsaturated nitrile derivatives.<sup>9,10</sup> Moreover, a number of pesticidal heterocyclic compounds were synthesized from  $\alpha$ , $\beta$ -unsaturated nitriles as synthons.



**RESULTS AND DISCUSSION** 

The required acrylonitrile 1 was synthesized adopting the method of Saito et al,<sup>11</sup> and was treated with

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methoxycarbonylmethylenetriphenylphosphorane 2a in refluxing toluene containing triethylamine to give 3-aryl-4-cyano-1-oxopyrido[2,1,b][1,3]benzothiazole<sup>12</sup> 6, (54%) and the new ylide 7 (18%). The pyridone derivative 6 was again obtained in a better yield (68%) as the sole reaction product when a mixture of 1 and 2b was refluxed in toluene containing triethylamine.

The structure of the orange crystalline product 6 is supported by: i) the correct elemental analysis and molecular weight determination; ii) its IR spectrum showed the characteristic bands at 2232 and 1686 cm<sup>-1</sup> due to the nitrile and the tertiary amide groups and the disappearance of the bands at 1610 and 1428 cm<sup>-1</sup> due to -C=CHAr and -N=C-S- absorptions;<sup>13</sup> iii) the <sup>1</sup>H-NMR showed the absence of the signal at  $\delta$  8.45 ppm for the exocyclic methine proton<sup>11</sup> and the appearance of only a multiplet in the range  $\delta$  7.46 - 8.25 ppm, and iv) its <sup>13</sup>C-NMR spectrum showed carbon signals at  $\delta$  112.2 (C-CN), 118.7 (C-CN) and at 172.5 ppm (C=C), amide).<sup>14</sup>

The ylide structure 7 ( $\delta p$ = 22.35 ppm) is assigned from its molecular weight measurement, its infrared absorption at 1723 cm<sup>-1</sup> (C=O, ester) and its <sup>1</sup>H-NMR spectrum which showed the methoxyl protons at  $\delta$  3.73 ppm. Each of the exocyclic methine protons (2H, *AB* system) in 7 appeared as a doublet of doublet. That of proton **a** (P-C-CH) was centered at  $\delta$  3.66 with <sup>3</sup>J<sub>HP</sub>= 10.5 Hz, whilst the other proton **b** (-P-C-CH-CH) was centered at  $\delta$  3.98 ppm with <sup>4</sup>J<sub>HP</sub> = 6.2 Hz. In its <sup>13</sup>C-NMR spectrum, signals were observed at  $\delta$  54.3 (OCH<sub>3</sub>) and at 126.6 ppm (d, J<sub>CP</sub>= 98.4 Hz, C=P).



A possible explanation of the production of the ylide 7 and the pyrido-derivative 6 is presented in Scheme 1. Initial Michael addition of the carbanion center in the Wittig reagent 2a, to the more electrophilic site of the exocyclic, ethylenic linkage in 1 affords the resonance hybrid 4 which may stabilize itself in two ways: 1. By internal Hofmann elimination of triphenylphosphine, followed by an intramolecular cyclization of the intermediate 5, which gives the pyridone-derivative 6 via the extrusion of a suitable moiety (i.e. RH, R = OCH<sub>3</sub> or OC<sub>2</sub>H<sub>5</sub>). 2. Through proton migration from  $\alpha$ - to  $\gamma$ -carbon atom, giving rise to the new ylide 7<sup>15</sup> (only with 2a). Attempts for thermal intramolecular cyclization of the prepared ylide 7 were also made. When 7 was heated above its melting point at 210 °C, it was gradually transformed into intractable material. On the other hand, compound 7 was recovered unchanged after prolonged boiling in toluene. This intramolecular unreactivity of 7 and the formation of the cyclic- 6 and the acyclic- 7 products in the above reactions appears to be dependent on the spatial arrangement of the reactive groups in the polar addition intermediates 4a, b.

Treatment of the acrylonitrile 1 with acetylmethylenetriphenylphosphorane 2c in boiling dry toluenc containing triethylamine gave the new ylide 10 in ~78% yield according to the recorded mass spectrum and the analytical data. The ylide structure was confirmed by a signal at  $\delta$  19.94 ppm in the <sup>31</sup>P-NMR spectrum, and the presence of a doublet (*Jcp*= 97.5 Hz) at 131.7 ppm assigned for C=P in its <sup>13</sup>C-NMR spectrum and the absence of a nitrile group absorption in its IR spectrum. The reaction may be viewed as occurring *via* Michael

#### Scheme 2



addition of 2c to the carbon-carbon double bond activated by electronegative nitrile group to give the betaine 8. Elimination of the nitrile group affords the phosphonium salt 9 which then loses HCN to give the new stable phosphorane 10 (Scheme 2). Such a mechanism parallels the reaction path previously reported by Trippett<sup>16</sup> for the reaction of tetracyanoethylene and  $\beta$ -ketoalkylidenephosphoranes. It was of interest to explore the synthetic usefulness of the alkylated phosphorane 10. When ylide 10 was allowed to react with aromatic aldehydes (e.g., *p*-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CHO), in the presence of sodium ethoxide, the Wittig reaction readily occurred and gave the expected Wittig product 11. The structure of 11 was established from its elemental analysis and spectral properties (*cf.* experimental) which are consistent with the assigned structure.

When the  $\alpha,\beta$ -unsaturated nitrile 1 was treated with an equimolar amount of benzoylmethylenetriphenylphosphorane (2d) under the same reaction conditions described for 2a-c, products 12a (~22%), 14 (~38%) and 15 (~14%) were obtained. This result is based on analytical and spectroscopic interpretations (see experimental). Thus, for example, combustion values and molecular weight determination (MS) for the cyclopropene derivative 15 corresponded to C<sub>23</sub>H<sub>15</sub>NOS, its IR spectrum showed bands at 1656 (C(O), benzoyl) and 1640 (C=C, cyclopropene); its <sup>1</sup>H-NMR spectrum showed only a multiplet (14H) in the range  $\delta$ 7.25-7.92 due to the aromatic protons alongwith a singlet (1H) at 2.88 ppm due to the cyclopropene methine proton and its <sup>13</sup>C-NMR spectrum showed carbon signals at  $\delta$  42.4 (CHAr), 133.4 (C-Bz), 150.7 (C=CBz) and 194.6 ppm (C(O), benzoyl). It is reasonable to assume that the initial dipolar structure 4cA, formed from 1 and 2d is present with its resonance form 4cB (Scheme 3). Stabilization of 4cA is achieved *via* the migration of the  $\alpha$ -proton to the electron rich center of the molecule (Hofmann transylidation)<sup>17</sup> to give the new ylide 12a, a tautomer form of its analog 7. Conversely, formation of the cyclopropene derivative 15 can be interpreted by intramolecular cyclization of the betaine 4cB via elimination of triphenylphosphine and hydrogen cyanide.<sup>15b,18</sup> On the other hand, formation of the pyran-imine 14 (moderately stable) can be explained via an internal Hofmann elimination of triphenylphosphine from the betaine 4cB accompanied by spontaneous  $\delta$ -lactonization of the intermediate 13 (Scheme 3). The latter step of transformation of the nitrile group to an imino- group has already been reported to proceed through an intramolecular cyclization of 1,3-benzothiazole compounds with extended conjugation;<sup>11,19</sup> similar to the intermediates 4c and 13.



We next studied the reaction of the substrate 1 with formylmethylenetriphenylphosphorane (2e). A mixture of 1 and 2e, prepared *in situ* from the corresponding chloride salt, in toluene containing triethylamine was heated under reflux for 45 h and the product mixture was then separated by column chromatography to give besides the parallel compound 12b (30%), the pyridone 16 (19%) and 18 (14%). When the same reaction was carried out in boiling ethyl alcohol containing triethylamine, only compounds 12b (22%) and 16 (15%) were obtained. The structure of the ylide 12b ( $\delta p$ = 21.4 ppm) has been deduced from its elemental analysis and its NH band at 3220 cm<sup>-1</sup> and its carbonyl peak at 1723 cm<sup>-1</sup>; its <sup>1</sup>H-NMR signals at  $\delta_H$  3.85 (d, <sup>3</sup>J<sub>HP</sub>= 10.5 Hz, CHAr), 8.66 (s, NH, exchangeable with D<sub>2</sub>O) and at 9.54 ppm (d, <sup>3</sup>J<sub>HP</sub> = 8.9 Hz, CHO).

The structure of 16 is confirmed from its spectroscopic data. Its IR spectrum indicates that 16A is tautomeric with 16B, since a strong broad band appears at 3455 cm<sup>-1</sup> due to free OH in 16B and a sharp and strong band appears at 1680 cm<sup>-1</sup> due to a carbonyl group in 16A. The <sup>1</sup>H-NMR spectrum is not that simple due to the appearance of the common features of 16A and 16B. The methylene protons in 16A are nonequivalent and the shift between them are small compared with the geminal coupling constant. Thus, the *AB* system pattern is quite distorted, and the net result is three peaks in the range  $\delta$  2.35-2.38 ppm. The methine proton absorption consists of two pairs at 3.26-3.39 ppm. The spectrum showed also two signals at  $\delta$ 

3.78 and 4.76 ppm due to the benzyl and hydroxyl protons in 16B. However, the structure of 16 was confirmed form <sup>13</sup>C-NMR data which is consistent with the equilibrium 16A - 16B and showed signals among others, at  $\delta c$  29.2 (CH<sub>2</sub>), 150.7 (COH) and at 173.5 ppm (C=O, amide). However, the results of the spectroscopic interpretation for 16 indicate that both the pyridone form 16A and its enol tautomer 16B present in equilibrium although structure 16A which possesses an amide grouping, should be much more stable and in turn more preferable, at least in the solid state, than the enol form 16B.

Scheme 4



Compound 18 was found to be a constitution-isomer but not identical with structure 16 for the following reasons: the appearance of OH absorption at 3435 cm<sup>-1</sup> and the nearly complete disappearance of the carbonyl band; its <sup>1</sup>H-NMR spectrum showed the benzylic proton as a doublet ( $J_{HH}$ =1.8 Hz) at  $\delta$  4.45 due to allylic coupling with the vinyl proton on C-1 which appeared as an ill defined doublet at 6.33. The signal presented at 5.27 (1H) was attributable to the proton of the OH group. The distinguishing features of the <sup>13</sup>C-NMR spectrum of 18 were the presence of signals at 27.2 (CHAr), 114.8 (CN), 120.6 (C-CN) and 153.4 ppm (C-OH).

The reaction of 1 and 2e, however, may be viewed as occurring via the attack of 2e on the benzylidene double bond in two forms (Scheme 4): a) the ylidic form to produce 4d (Scheme 3, R=H) followed by proton migration, yielding 12b (R=H) or undergoes intramolecular cyclization through elimination of triphenyl-phosphine to give 16 which may be presented by the equilibrium 16A -16B, b) the reduced form of the aldehydic function, invoked by the basic medium and the substrate 1, to give the intermediate 17 which is then intramolecular cyclized with elimination of triphenylphosphine to afford the pyridine derivative 18. Such reduction of the aldehydic group has been amply documented<sup>20</sup> and we have invoked it on several occasions<sup>21,22</sup> to rationalise our experimental findings.

This work was also extended to the arylidenephosphorane system. In contrast to the above series of the Wittig reagents (2a-e) which undergo several competing processes with 1 leading to different products, diphenylmethylenetriphenylphosphorane 3 reacts smoothly with the benzylidene 1, through one reaction pathway, and gives the cyclopropane derivative 19 in a high yield (68%) (Scheme 5).<sup>18</sup> The structure is indicated by its light brown colour; its molecular weight; its strong IR absorptions at 2210 (CN) and 1435 (-N=C-S); its <sup>1</sup>H-NMR absorption at  $\delta$  7.42-8.22 (m, 19H, Ar-H) and 4.17 (s, 1H, benzyl-H) and its <sup>13</sup>C-NMR

absorption at δ 30.4 (CHAr), 45.5 (C-CN), 48.7 (C-Ph<sub>2</sub>) and 110 ppm (CN).



In conclusion, the reactions of the  $\alpha$ , $\beta$ -unsaturated nitrile 1 with stabilized Wittig reagents provide an easy route for the preparation not only of the previously reported<sup>15,16</sup> new ylides, similar to 7 or 10, but also of fused-pyridine derivatives (e.g. 6, 16 and 18); pyran- 14, cyclopropene- 15 and cyclopropan- 19 derivatives possessing the benzothiazolyl grouping. The results also indicated that polarity and temperature effects play only a very limited role. The substituents of the ylides, on the other hand, seem to be crucial. Moreover, the feature common to all of these interactions, as stated before,<sup>11,19</sup> is the tendency of the thiazole nucleus to establish a fused pyridine ring.

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### **EXPERIMENTAL**

Melting points are uncorrected, IR spectra were obtained with a Perkin-Elmer 297 in KBr. <sup>1</sup>H- and <sup>13</sup>C-NMR spectra were recorded in CDCl<sub>3</sub> or [D<sub>6</sub>]DMSO as a solvent on a Joel-270 MHz spectrometer, with SiMe<sub>4</sub> as internal standard. <sup>31</sup>P-NMR spectra were taken with a Varian CFT-20 (vs. external 85% H<sub>3</sub>PO<sub>4</sub>). Mass spectra were determined at 70 eV on a Shimadzu GCS-QP 1(X)) EX spectrometer provided with a data system. Compound 1 was prepared as previously reported. <sup>11</sup>

**Reaction of 2-Benzylidenecyanomethyl-1,3-benzothiazole 1 with methoxy- 2a and ethoxy**carbonylmethylenetriphenylphosphorane 2b. A solution of 1 (1.3 g, 5 mmol) and 2a (2.3 g, 7 mmol) in toluene (50 ml) containing triethylamine (TEA, 0.7 ml) was refluxed for 3 days. After evaporation of the solvent, the remainder was subjected to column chromatography [silica gel, light petroleum/CHCl<sub>3</sub> (9:1) with increasing amounts of CHCl<sub>3</sub> (up to 100%) and then with pure ethyl acetate].

4-Cyano-1-oxo-3-phenylpyrido-3-phenyl[2,1-b][1,3]benzothiazole 6 was eluted first (7:3, v/v) as orange crystals (0.88 g, 53.8%), m.p. 88.5 °C (pentane). -IR (KBr): v 2232 (CN), 1686 cm<sup>-1</sup> (C=O); -NMR (CDCl<sub>3</sub>):  $\delta_{\rm H}$  7.46-8.25 ppm (m, 10H, Ar-H and pyridine-H), - $\delta_{\rm C}$  112.2 (C-CN), 118.7 (CN), 172.5 ppm (C(O), amide); -MS: m/z (%) = 302 (33) [M<sup>+</sup>], 276 (100).

C<sub>18</sub>H<sub>10</sub>N<sub>2</sub>OS (302.36) : Calcd. C 71.50 H 3.33 N 9.26 S 10.61 Found: C 71.58 H 3.27 N 9.22 S 10.56 *Methyl* 4-(1,3-benzothiazol-2-yl)-4-cyano-3-phenyl-2-triphenylphosphorylidenebutan-1-oate 7 was eluted secondly (AcOEt) as light brown crystals (530 mg, 18.2%), m.p. 195-197 °C (benzene); -IR (KBr):  $\upsilon$  2232 (CN), 1723 (C=O, ester), 1680, 1510 (C=P); 1428 (-N=C-S-), 1400, 980 cm<sup>-1</sup> (P-C, phenyl); -NMR (CDCl<sub>3</sub>) :  $\delta_{\rm H}$  3.66 (d,  ${}^{3}J_{HP}$  = 10.5 Hz, CHa), 3.73 (s, 3H, OCH<sub>3</sub>), 3.98 (d,  $J_{HP}$  = 6.5 Hz, -CHb); 7.2-8.2 ppm (m, 24H, Ar-H), - $\delta$ c 28.7, 33.3 (CH-CH), 52.5 (OCH<sub>3</sub>), 126.6 (d,  $J_{CP}$  = 98.4 Hz, C=P), 169.2 ppm (C=O), - $\delta$ p = 22.35 ppm; -MS : m/z (%) = 596 (12) [M<sup>+</sup>].

C<sub>37</sub>H<sub>29</sub>N<sub>2</sub>O<sub>2</sub>PS (596.7) Calcd. C 74.48 H 4.90 N 4.69 P 5.19 S 5.37 Found: C 74.55 H 4.86 N 4.63 P 5.24 S 5.47

Triphenylphosphine and triphenylphosphine oxide were also isolated and identified.

When the same reactions were carried out without TEA, the educts (1 + 2a,b) were recovered practically unchanged (>80%).

When 1 (1.3 g, 5 mmol) was allowed to react with 2b (2.4 g, 7 mmol) under above same conditions and working up, only compound 6 (1 g, 68.3%) was isolated and characterised (m.p., mixed m.ps. and comparative spectra).

Action of heat on the ylide 7: Method A: -A small amount of 7 was heated to its melting point temperature for 5 min in an oil bath (temperature was maintained 10 °C over melting point). After cooling, the residue was extracted with hot hexane. The solid material that crystallised out upon cooling was filtered off to give colourless crystals proved to be triphenylphosphine. Hexane insoluble residue afforded only an unidentified resinous mass, mp > 350 °C.

Method B: -A sample of 7 (0.25 g) was refluxed in toluene for 30 h. After evaporation of the solvent in vacuo, the orange solid was collected (>90%) with small amount of diethyl ether and shown to be identical with 7 (TLC and comparative IR and mass spectra).

**Reaction of 1** with (acetylmethylene) triphenylphosphorane 2c: A mixture of 1 (1.3 g, 5 mmol) and 2c (2.2 g, 7 mmol) was refluxed in toluene (50 ml) containing TEA (0.7 ml) for 3 days. The solvent was evaporated under reduced pressure and the remainder was chromatographed on silica gel using hexane containing increasing amounts of chloroform.

5-Phenyl-4-(1,3-benzothiazol-2-yl)-3-triphenylphosphoranylidenepent-4-en-2-one 10: was eluted (8:2 v/v) as golden yellow crystals (2.2 g, 78.7%), m.p. 102-104 °C (cyclohexane), -IR (KBr): υ 1715 (C=(), acetyl), 1675, 1515 (C=P), 1610 (C=CHAr), 1425 (-N=C-S-), 1410, 980 cm<sup>-1</sup> (P-C, phenyl); -NMR (CDCl<sub>3</sub>):  $\delta_{11}$  2.09 (d,  $J_{HP}$  = 6.8 Hz, 3H, C(O)CH<sub>3</sub>), 7.22-8.25 (m, 24H, Ar-H), 8.47 ppm (d,  $J_{HP}$  = 4.6 Hz, =CHAr), -δc 24.7 (CH<sub>3</sub>), 118.6 (CHAr), 131.7 (d,  $J_{HP}$  = 97.5 Hz, C=P), 140.2 (-C-C=P), 183.2 (C=O), -δp = 19.94 ppm; -MS: m/z (%) = 553 (52) [M<sup>+</sup>].

C<sub>36</sub>H<sub>28</sub>NOPS (553.7) Calcd. C 78.09 H 5.10 N 2.53 P 5.60 S 5.79 Found: C 78.17 H 4.96 N 2.48 P 5.52 S 5.68

Wittig reaction of the produced ylide 10: To a solution of 10 (0.5 g, 0.9 mmol) in ethyl acetate (30 ml)

containing sodium hydroxide (0.1 g, 10 mmol), p-nitrobenzaldehyde (0.15 g, 10 mmol) was added. The reaction mixture was refluxed for 15 h. The product mixture was concentrated to 15 ml, diluted with 20 ml dist. water, acidified with conc. HCl and then extracted with two- 100 portions of CHCl<sub>3</sub>. The chloroform extracts were combined, dried over anhydrous MgSO<sub>4</sub> and evaporated *in vacuo* under reduced pressure. The residue was chromatographed on silica gel with hexane-CHCl<sub>3</sub> (8:2 v/v) to give the Wittig product 11 as colourless needles (285 mg, 74%), m.p. 80-82 °C (light petroleum b.r. 40-60 °C), -IR (KBr): v 1715 (C=(), acetyl), 1615, 1605 (C=C, exocyclic), 1520 cm<sup>-1</sup> (NO<sub>2</sub>); -<sup>1</sup>H-NMR (CDCl<sub>3</sub>) :  $\delta$  2.21 (s, 3H, CH<sub>3</sub>, acetyl), 7.05 - 8.33 ppm (m, 15H, Ar-H & 2=CH, benzylidenes); -MS : m/z (%) = 426 (48) [M<sup>+</sup>].

C<sub>25</sub>H<sub>18</sub>N<sub>2</sub>O<sub>3</sub>S (426.5) Calcd. C 70.4 H 4.25 N 6.56 S 7.52 Found: C 70.46 H 4.18 N 6.43 S 7.47

**Reaction of 1 with benzoylmethylenetriphenylphosphorane 2d:** -A mixture of 1 (1.3 g, 5 mmol) and **2d** (2.7 g, 7 mmol) was refluxed in toluene (70 ml) containing TEA (1 ml) for 3 days, the procedure and the working up were the same as described for **2a** whereby elution up to 6:4 light petroleum (b.r 60-80)  $^{\circ}$ C)-CHCl<sub>3</sub>, yielded TPP and TPPO.

Elution with light petroleum (b.r. 60-80 °C)-CHCl<sub>3</sub> (1:1 v/v) afforded 2 (1-cyano-2,2,3-triphenylcyclopropen -1-yl)[1,3]benzothiazole 15 (255 mg, 14.6%) as pale yellow crystals, m.p. 70-72 °C (light petroleum, b.r. 40-60 °C), -IR (KBr):  $\upsilon$  1656 (C=O),<sup>23</sup> 1640 (C=C, cyclopropene), 1425 cm<sup>-1</sup>, (N=C-S); -NMR (CDCl<sub>3</sub>):  $\delta_{\rm H}$  2.88 (s, 1H, -CHAr), 7.25-7.92 ppm (m, 14 H, Ar-H);  $\delta_{\rm C}$ : -42.4 (CHAr), 133.4 (C-Bz), 150.7 (C=C Bz), 194.6 ppm (C(O), benzoyl); -MS: m/z (%) = 353 (28) [M<sup>+</sup>].

C<sub>23</sub>H<sub>15</sub>NOS (353.4) Calcd. C 78.16 H 4.28 N 3.96 S 9.07 Found: C 78.25 H 4.22 N 3.87 S 8.94

Elution with light ptroleum (b.r. 60-80 °C)-chloroform (4:6 v/v) yielded 3-(1,3-benzothiazol-2-yl)-4,6-diphenyl-2-iminopyran 14 (724 mg, 38.4%), m.p. 98-100 °C (pentane), -IR (KBr) :  $\upsilon$  3155 (NH, weak), 1660 (C=NH), 1065 (C=C-O), 1430 cm<sup>-1</sup> (N=C-S); -NMR (CDCl<sub>3</sub>) :  $\delta_{\rm H}$  5.65 (s, 1H, =NH), 7.43 - 8.2 ppm (m, 15H, Ar-H and pyran-H), - $\delta$ c 146.4 (C=NH), 151.7 ppm (-O-CPh); -MS: m/z (%) = 380 (20) [M<sup>+</sup>].

 $C_{24}H_{16}N_2OS~(380.5~)~Calcd.~C~75.76~H~4.24~N~7.36~S~8.43 \\ Found:~C~75.82~H~4.17~N~7.29~S~8.40 \\$ 

Elution with light petroleum (b.r. 60-80 °C)-chloroform (1:1 v/v) eluted 3-(3H-1,3-benzothiazol-2-yl)-3-cyano-2-phenyl-1-benzoyl-1-triphenylphosphoranylideneprop-1,3-diene **12a** (707 mg, 22.3%), m.p. 154 -156 °C (CHCl<sub>3</sub>), -IR (KBr):  $\upsilon$  3280 (NH), 2211 (CN), 1680, 1510 (C=P), 1655 (C=O), 1400, 980 (P-C, phenyl); -NMR (CDCl<sub>3</sub>):  $\delta_{\rm H}$  4.22 (d,<sup>3</sup>J<sub>HP</sub> = 8.5 Hz, 1H, ArCH), 6.84 (s, 1H, NH), 7.35-8.26 ppm (m, 29H, Ar-H),  $\delta$ c-28.7 (CHAr), 110.4 (C-CN), 118.2 (CN), 131.3 (d, J<sub>C-P</sub> = 84.8, C=P), 192.8 (C(O)Ph); - $\delta$ p = 21.3 ppm; -MS : m/z (%) = 642 (18) [M<sup>+</sup>].

C<sub>42</sub>H<sub>31</sub>N<sub>2</sub>OPS (642.8) Calcd. C 78.48 H 4.86 N 4.36 P 4.82 S 4.99 Found: C 78.53 H 4.82 N 4.31 P 4.94 S 4.86

**Reaction of 1with formylmethylenetriphenylphosphorane 2e:** - A mixture of 1 (1.3 g, 5 mmol) and 2e, chloride salt, (2.4 g, 7 mmol) was refluxed in toluene (70 ml) containing TEA (1 ml) for 2 days and the

product mixture was worked up, as described before for 2a. Chromatography on silica gel with hexane -CHCl<sub>3</sub> (1:1 v/v) as eluent gave orange crystals of compound 16 (280 mg, 18.7%), m.p. 130 °C (acetone-pentane), -IR (KBr):  $\upsilon$  3455 (br. OH), 2201-2210 (br. CN), 1680 cm<sup>-1</sup> (C=O); -NMR (DMSO) : 16A :  $\delta_H$  2.36-2.38 (2d, distorted, 2H, -CH<sub>2</sub>), 3.26-3.37 (two pairs, 1H, -CHAr); 16B: 3.78 (s, 1H, -CHAr), 4.73 ppm (s, OH, exchangeable with D<sub>2</sub>O), 7.26-8.08 (m, 5H, Ar-H & pyridine-H); - $\delta_C$  29.2 (CH<sub>2</sub>), 33.5 (CHAr), 108.4 (C-CN), 118.7 (CN), 150.7 (C-OH), 173.5 ppm (C=O, amide); -MS: m/z (%) = 304 (100 [M<sup>+</sup>].

C<sub>18</sub>H<sub>12</sub>N<sub>2</sub>OS (304.4) Calcd. C 71.03 H 3.97 N 9.20 S 10.53

Found: C 71.12 H 3.88 N 9.14 S 10.44

Elution with acetone afforded two fractions. The first fraction yielded yellow crystals of 4-(3H-1,3-benzothiazolidene)-4-cyano-3-phenyl-2-triphenylphosphoranylidene-butan-1-al 12b (843 mg, 30%), m.p. 148-150 °C (acetonitrile), -IR (KBr): v 3320 (NH), 2211 (CN), 1723 (C=O), 1675, 1515 cm<sup>-1</sup> (C=P); -NMR (DMSO):  $\delta_{\rm H}$  3.85 (d,  ${}^{3}J_{HP}$  = 10.5 Hz, 1H, CHAr), 8.66 (s, 1H, NH, exchangeable with D<sub>2</sub>O), 7.33-8.24 (m, 24H, Ar-H), 9.54 ppm (d,  ${}^{3}J_{HP}$  = 8.7 Hz, 1H, CHO), - $\delta_{\rm C}$  27.6 (CHAr), 128.8 (d,  $J_{CP}$  = 88.4 Hz, C=P), 184.8 ppm (CHO), - $\delta_{\rm P}$  = 21.4 ppm; -MS : m/z (%) = 566 (75) [M<sup>+</sup>].

C<sub>36</sub>H<sub>27</sub>N<sub>2</sub>OPS (566.7) Calcd. C 76.30 H 4.80 N 4.94 P 5.46 S 5.66 Found: C 76.37 H 4.72 N 4.84 P 5.39 S 5.61

The second fraction gave yellow crystals of 4-cyano-2-hydroxy-3H-3-phenyl-pyrido [2,1-b] [1,3]benzothiazole 18 (214 mg, 14.3%), m.p. 105-107 °C (cyclohexane), -IR (KBr) :  $\upsilon$  3455 (OH), 2218 cm<sup>-1</sup> (CN); -NMR (DMSO) :  $\delta_{\rm H}$  4.45 (d,  $J_{HH}$ =1.8 Hz, 1H, CHAr), 5.27 (s, 1H, OH, exchangeable with D<sub>2</sub>O), 6.33 (d, ill-defined, 1H, N-CH), 7.33-7.96 (m, 9H, Ar-H); - $\delta$ c 27.2 (CHAr), 114.8 (CN), 120.6 (C-CN), 153.4 ppm (C-OH); -MS: m/z (%) = 304 (55) [M<sup>+</sup>].

$C_{18}H_{12}N_2OS$	(304.4)	Calcd.	C 71.03	H 3.97	N 9.2	S 10.53
		Found:	C 71.11	H 3.93	N 9.12	S 10.5

TPP and TPPO were also isolated and identified from this reaction. When the same reaction was repeated in refluxed ethyl alcohol containing TEA (50 h). Compounds 12b (22%) and 16 (15%) were again obtained and characterised.

**Reaction of 1 with diphenylmethylenetriphenylphosphorane 3:** Into a well dried three-necked flask containing 0.5 g sodium metal dissolved in 50 ml absolute alcohol, ylide **3** (bromide salt) (3 g, 6 mmol) was added portionwise. The reaction mixture was stirred at room temperature for 1 h followed by addition of 1 (1.3 g, 5 mmol) portionwise within 30 min. and then heated under reflux for 24 h. The product mixture was concentrated to 20 ml, diluted with 20 ml dist. water, acidified with conc. HCl and then extracted with two-100 portions of CHCl<sub>3</sub>. The CHCl<sub>3</sub> extracts were combined, backwashed with 100 ml of H<sub>2</sub>O, dried over anhydrous MgSO<sub>4</sub>, and evaporated *in vacuo* under reduced pressure. The residue was chromatographed on silica gel with hexane-chloroform. Elution with pure hexane afforded TPP. Fraction up to (7:3 v/v) eluted light brown crystals of 2-(*1-cyano-2,2,3-triphenylcycloprop-1-yl)-1,3-benzothiazole* **19** (1.5 g, 72%), m.p. 170-172 "C (benzene), -IR (KBr):  $\upsilon$  2210 cm<sup>-1</sup> (CN); -NMR (CDCl<sub>3</sub>) :  $\delta_{\rm H}$  4.17 (s, 1H, CHAr), 7.42-8.22 ppm (m, 19H, Ar-H), - $\delta_c$  30.4 (CHAr), 45.5 (C-CN), 48.7 (C-Ph<sub>2</sub>), 110 ppm (CN); -MS: *m/z* (%) = 428 (8) [M<sup>+</sup>].

 $C_{29}H_{20}N_2S$  (428.6) Calcd. C 81.27 H 4.70 N 6.54 S 7.48 Found: C 81.22 H 4.62 N 6.47 S 7.41

No reaction was observed when the same reaction (1+3) was carried out in boiling toluene containing TEA even after 4 days.

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