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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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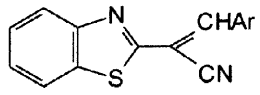
Abstract : The behaviour of the acrylonitrile **1** toward different types of phosphorus ylides such as alkoxycarbonyl- **2a,b** and β-keto-alkylidene phosphoranes **2c-e** as well as arylidenephosphorane **3** has been studied. The reactions take different pathways leading to unusual products, depending 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.

INTRODUCTION

In connection with other investigations,[1-6] we were interested in determining how well the reaction proceeds between α,β-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 β-keto-methylenetriphenylphosphoranes **2c-e** as well as arylidene- phosphorane **3**. The incentive in this direction is based upon recorded potencies of the thiazole nucleus[7,8] and of the unsaturated nitrile derivatives.[9,10] Moreover, a number of pesticidal heterocyclic compounds were synthesized from α,β-unsaturated nitriles as synthons.



1, Ar = C_6H_5

$Ph_3P{=}CHCOR$

$Ph_3P{=}C(C_6H_5)_2$

3

2	R	2	R
a	OCH_3	d	C_6H_5
b	OC_2H_5	e	H
c	CH_3		

RESULTS AND DISCUSSION

The required acrylonitrile **1** was synthesized adopting the method of Saito et al,[11] and was treated with

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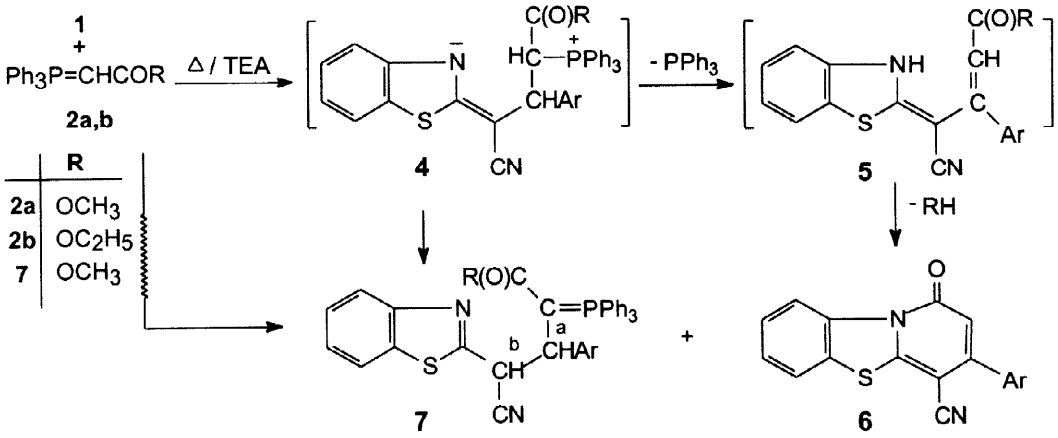
methoxycarbonylmethylenetriphenylphosphorane **2a** in refluxing toluene containing triethylamine to give 3-aryl-4-cyano-1-oxopyrido[2,1,*b*][1,3]benzothiazole[12] **6**, (54%) and the new ylide **7** (18%). The pyridone derivative **6** was again obtained in a better yield (68%) as the sole reaction 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^{-1} due to the nitrile and the tertiary amide groups and the disappearance of the bands at 1610 and 1428 cm^{-1} due to -C=CHAr and -N=C-S- absorptions;[13] iii) the ^{1}H-NMR showed the absence of the signal at δ 8.45 ppm for the exocyclic methine proton[11] and the appearance of only a multiplet in the range δ 7.46 - 8.25 ppm, and iv) its ^{13}C-NMR spectrum showed carbon signals at δ 112.2 (C-CN), 118.7 (C-CN) and at 172.5 ppm (C=O, amide).[14]

The ylide structure **7** (δp= 22.35 ppm) is assigned from its molecular weight measurement, its infrared absorption at 1723 cm^{-1} (C=O, ester) and its ^{1}H-NMR spectrum which showed the methoxyl protons at δ 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 δ 3.66 with $^3J_{HP}$= 10.5 Hz, whilst the other proton **b** (-P-C-CH-**CH**) was centered at δ 3.98 ppm with $^4J_{HP}$ = 6.2 Hz. In its ^{13}C-NMR spectrum, signals were observed at δ 54.3 (OCH_3) and at 126.6 ppm (d, J_{CP}= 98.4 Hz, C=P).

Scheme 1

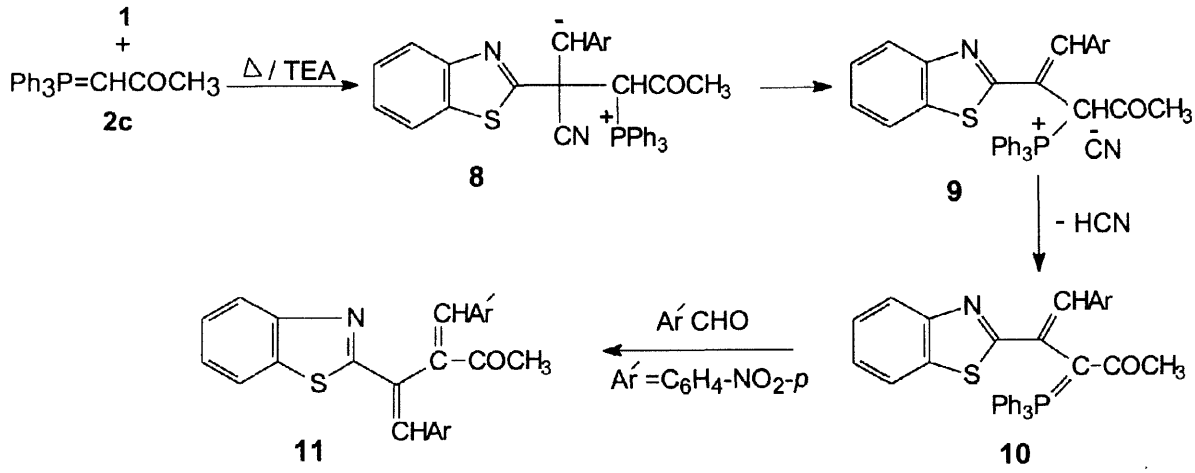


A possible explanation of the production of the ylide **7** and the pyrido-derivative **6** is presented in Scheme 1. Initial Michael addition of the carbanion center in the Wittig reagent **2a**, to the more electrophilic site of the exocyclic, ethylenic linkage in **1** affords the resonance hybrid **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_3 or OC_2H_5). 2. Through proton migration from α- to γ-carbon atom, giving rise to the new ylide **7**[15] (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 toluene 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 δ 19.94 ppm in the ^{31}P-NMR spectrum, and the presence of a doublet (*Jcp*= 97.5 Hz) at 131.7 ppm assigned for C=P in its ^{13}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

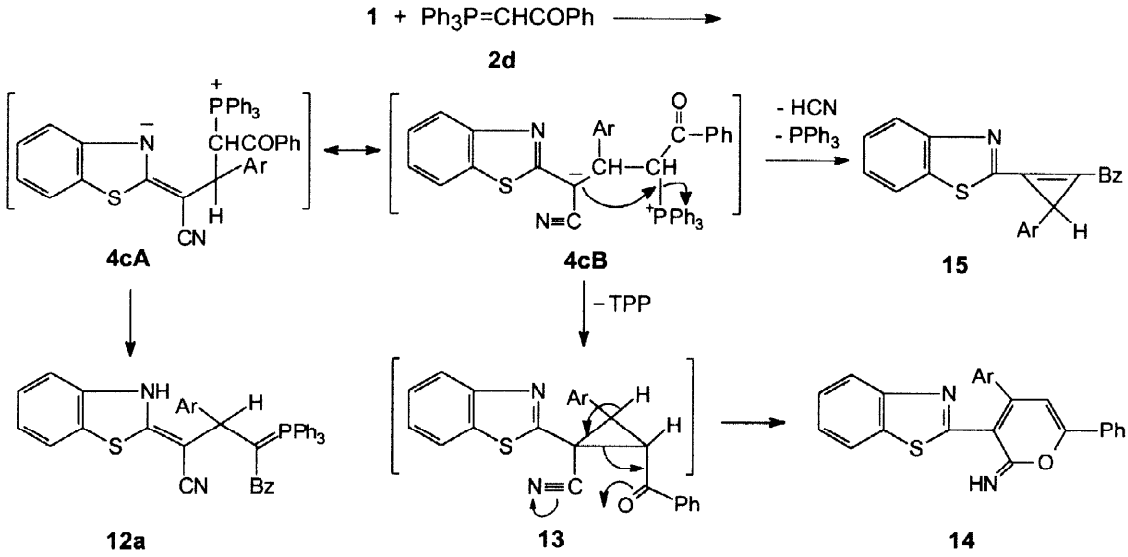


addition of **2c** to the carbon-carbon double bond activated by electronegative nitrile group to give the betaine **8**. Elimination of the nitrile group affords the phosphonium salt **9** which then loses HCN to give the new stable phosphorane **10** (Scheme 2). Such a mechanism parallels the reaction path previously reported by Trippett[16] for the reaction of tetracyanoethylene and β-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*-$NO_2C_6H_4CHO$), 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 α,β-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 $C_{23}H_{15}NOS$, its IR spectrum showed bands at 1656 (C(O), benzoyl) and 1640 (C=C, cyclopropene); its ^{1}H-NMR spectrum showed only a multiplet (14H) in the range δ 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 ^{13}C-NMR spectrum showed carbon signals at δ 42.4 (**C**HAr), 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 α-proton to the electron rich center of the molecule (Hofmann transylidation)[17] 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.[15b,18] 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 δ-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;[11,19] similar to the intermediates **4c** and **13**.

Scheme 3

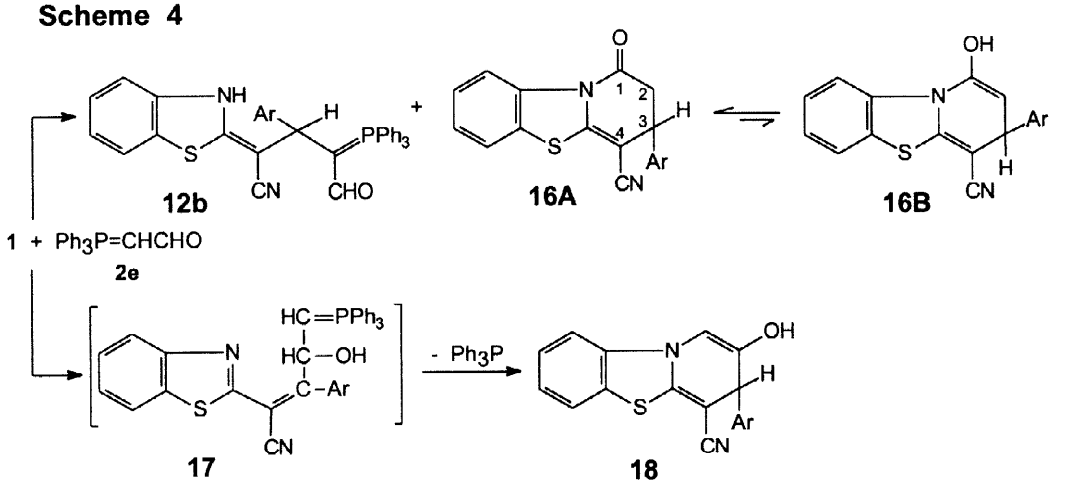


We next studied the reaction of the substrate **1** with formylmethylenetriphenylphosphorane (**2e**). A mixture of **1** and **2e**, prepared *in situ* from the corresponding chloride salt, in toluene containing triethylamine was heated under reflux for 45 h and the product mixture was then separated 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** (δp= 21.4 ppm) has been deduced from its elemental analysis and its NH band at 3220 cm^{-1} and its carbonyl peak at 1723 cm^{-1}; its ^{1}H-NMR signals at δ_H 3.85 (d, $^3J_{HP}$= 10.5 Hz, **CH**Ar), 8.66 (s, **NH**, exchangeable with D_2O) and at 9.54 ppm (d, $^3J_{HP}$ = 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^{-1} due to free OH in **16B** and a sharp and strong band appears at 1680 cm^{-1} due to a carbonyl group in **16A**. The ^{1}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 δ 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 δ

3.78 and 4.76 ppm due to the benzyl and hydroxyl protons in **16B**. However, the structure of **16** was confirmed form ^{13}C-NMR data which is consistent with the equilibrium **16A** ⇌ **16B** and showed signals among others, at δc 29.2 (CH_2), 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



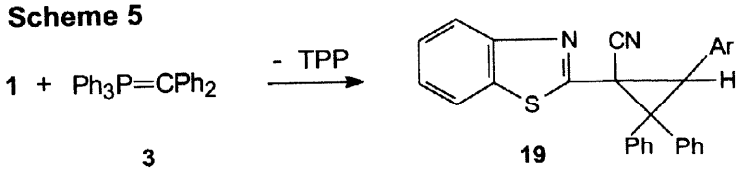
Compound **18** was found to be a constitution-isomer but not identical with structure **16** for the following reasons: the appearance of OH absorption at 3435 cm^{-1} and the nearly complete disappearance of the carbonyl band; its ^{1}H-NMR spectrum showed the benzylic proton as a doublet (J_{HH}=1.8 Hz) at δ 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 ^{13}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 triphenylphosphine 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[20] and we have invoked it on several occasions[21,22] 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).[18] 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 ^{1}H-NMR absorption at δ 7.42-8.22 (m, 19H, Ar-**H**) and 4.17 (s, 1H, benzyl-**H**) and its ^{13}C-NMR

absorption at δ 30.4 (**C**HAr), 45.5 (**C**-CN), 48.7 (**C**-Ph_2) and 110 ppm (CN).

Scheme 5



In conclusion, the reactions of the α,β-unsaturated nitrile **1** with stabilized Wittig reagents provide an easy route for the preparation not only of the previously reported[15,16] 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,[11,19] 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. ^{1}H- and ^{13}C-NMR spectra were recorded in $CDCl_3$ or [D_6]DMSO as a solvent on a Joel-270 MHz spectrometer, with $SiMe_4$ as internal standard. ^{31}P-NMR spectra were taken with a Varian CFT-20 (*vs.* external 85% H_3PO_4). Mass spectra were determined at 70 eV on a Shimadzu GCS-QP 1000 EX spectrometer provided with a data system. Compound **1** was prepared as previously reported.[11]

***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/$CHCl_3$ (9:1) with increasing amounts of $CHCl_3$ (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): υ 2232 (CN), 1686 cm^{-1} (C=O); -NMR ($CDCl_3$): δ_H 7.46-8.25 ppm (m, 10H, Ar-**H** and pyridine-**H**), -δc 112.2 (**C**-CN), 118.7 (**C**N), 172.5 ppm (**C**(O), amide); -MS: *m/z* (%) = 302 (33) [M^+], 276 (100).

$C_{18}H_{10}N_2OS$ (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): υ 2232 (CN), 1723 (C=O, ester), 1680, 1510 (C=P); 1428 (-N=C-S-), 1400, 980 cm^{-1} (P-C, phenyl); -NMR ($CDCl_3$) : δ_H 3.66 (d, $^3J_{HP}$ = 10.5 Hz, **CH**a), 3.73 (s, 3H, OCH_3), 3.98 (d, J_{HP} = 6.5 Hz, -**CH**b); 7.2-8.2 ppm (m, 24H, Ar-**H**), -δc 28.7, 33.3 (**CH-CH**), 52.5 (OCH_3), 126.6 (d, J_{CP} = 98.4 Hz, **C**=P), 169.2 ppm (**C**=O), -δp = 22.35 ppm; -MS : *m/z* (%) = 596 (12) [M^+].

$C_{37}H_{29}N_2O_2PS$ (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=O, acetyl), 1675, 1515 (C=P), 1610 (C=CHAr), 1425 (-N=C-S-), 1410, 980 cm^{-1} (P-C, phenyl); -NMR ($CDCl_3$): δ_H 2.09 (d, J_{HP} = 6.8 Hz, 3H, C(O)CH_3), 7.22-8.25 (m, 24H, Ar-**H**), 8.47 ppm (d, J_{HP} = 4.6 Hz, =**CH**Ar), -δc 24.7 (CH_3), 118.6 (**CH**Ar), 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^+].

$C_{36}H_{28}NOPS$ (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 $CHCl_3$. The chloroform extracts were combined, dried over anhydrous $MgSO_4$ and evaporated *in vacuo* under reduced pressure. The residue was chromatographed on silica gel with hexane-$CHCl_3$ (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): υ 1715 (C=O, acetyl), 1615, 1605 (C=C, exocyclic), 1520 cm^{-1} (NO_2); -^{1}H-NMR ($CDCl_3$) : δ 2.21 (s, 3H, CH_3, acetyl), 7.05 - 8.33 ppm (m, 15H, Ar-**H** & 2=**CH**, benzylidenes); -MS : *m/z* (%) = 426 (48) [M^+].

$C_{25}H_{18}N_2O_3S$ (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 °C)-$CHCl_3$, yielded TPP and TPPO.

Elution with light petroleum (b.r. 60-80 °C)-$CHCl_3$ (1:1 v/v) afforded *2 (1-cyano-2,2,3-triphenyl-cyclopropen -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): υ 1656 (C=O),[23] 1640 (C=C, cyclopropene), 1425 cm^{-1}, (N=C-S); -NMR ($CDCl_3$): δ_H 2.88 (s, 1H, -**CH**Ar), 7.25-7.92 ppm (m, 14 H, Ar-**H**); δc: -42.4 (**C**HAr), 133.4 (**C**-Bz), 150.7 (**C**=C Bz), 194.6 ppm (**C**(O), benzoyl); -MS: *m/z* (%) = 353 (28) [M^+].

$C_{23}H_{15}NOS$ (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) : υ 3155 (NH, weak), 1660 (C=NH), 1065 (C=C-O), 1430 cm^{-1} (N=C-S); -NMR ($CDCl_3$) : δ_H 5.65 (s, 1H, =N**H**), 7.43 - 8.2 ppm (m, 15H, Ar-**H** and pyran-**H**), -δc 146.4 (**C**=NH), 151.7 ppm (-O-**C**Ph); -MS: *m/z* (%) = 380 (20) [M^+].

$C_{24}H_{16}N_2OS$ (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 ($CHCl_3$), -IR (KBr): υ 3280 (NH), 2211 (CN), 1680, 1510 (C=P), 1655 (C=O), 1400, 980 (P-C, phenyl); -NMR ($CDCl_3$): δ_H 4.22 (d,$^3J_{HP}$ = 8.5 Hz, 1H, Ar**CH**), 6.84 (s, 1H, **NH**), 7.35-8.26 ppm (m, 29H, Ar-**H**), δc-28.7 (**C**HAr), 110.4 (**C**-CN), 118.2 (**C**N), 131.3 (d, $J_{C\text{-}P}$ = 84.8, **C**=P), 192.8 (**C**(O)Ph); -δp = 21.3 ppm; -MS : *m/z* (%) = 642 (18) [M^+].

$C_{42}H_{31}N_2OPS$ (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* 1*with 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 -$CHCl_3$ (1:1 v/v) as eluent gave orange crystals of compound **16** (280 mg, 18.7%), m.p. 130 °C (acetone-pentane), -IR (KBr): υ 3455 (br. OH), 2201-2210 (br. CN), 1680 cm^{-1} (C=O); -NMR (DMSO) : **16A** : δ_H 2.36-2.38 (2d, distorted, 2H, -CH_2), 3.26-3.37 (two pairs, 1H, -CHAr); **16B**: 3.78 (s, 1H, -CHAr), 4.73 ppm (s, OH, exchangeable with D_2O), 7.26-8.08 (m, 5H, Ar-H & pyridine-H); -δc 29.2 (CH_2), 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^+].

$C_{18}H_{12}N_2OS$ (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): υ 3320 (NH), 2211 (CN), 1723 (C=O), 1675, 1515 cm^{-1} (C=P); -NMR (DMSO): δ_H 3.85 (d, $^3J_{HP}$ = 10.5 Hz, 1H, CHAr), 8.66 (s, 1H, NH, exchangeable with D_2O), 7.33-8.24 (m, 24H, Ar-H), 9.54 ppm (d,$^3J_{HP}$ = 8.7 Hz, 1H, CHO), -δc 27.6 (CHAr), 128.8 (d, J_{CP} = 88.4 Hz, C=P), 184.8 ppm (CHO), -δ_P = 21.4 ppm; -MS : *m/z* (%) = 566 (75) [M^+].

$C_{36}H_{27}N_2OPS$ (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) : υ 3455 (OH), 2218 cm^{-1} (CN); -NMR (DMSO) : δ_H 4.45 (d, J_{HH}=1.8 Hz, 1H, CHAr), 5.27 (s, 1H, OH, exchangeable with D_2O), 6.33 (d, ill-defined, 1H, N-CH), 7.33-7.96 (m, 9H, Ar-H); -δc 27.2 (CHAr), 114.8 (CN), 120.6 (C-CN), 153.4 ppm (C-OH); -MS: *m/z* (%) = 304 (55) [M^+].

$C_{18}H_{12}N_2OS$ (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 $CHCl_3$. The $CHCl_3$ extracts were combined, backwashed with 100 ml of H_2O, dried over anhydrous $MgSO_4$, 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): υ 2210 cm^{-1} (CN); -NMR ($CDCl_3$) : δ_H 4.17 (s, 1H, CHAr), 7.42-8.22 ppm (m, 19H, Ar-H), -δc 30.4 (CHAr), 45.5 (C-CN), 48.7 (C-Ph_2), 110 ppm (CN); -MS: *m/z* (%) = 428 (8) [M^+].

$C_{29}H_{20}N_2S$ (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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