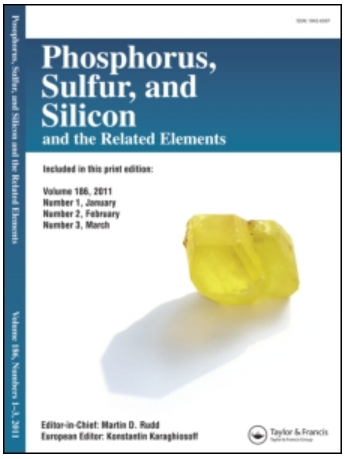

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SYNTHESIS AND REACTIONS OF 2-FURANYLIDENECYANOMETHYL-1,3-BENZOTHIAZOLE WITH TER- AND PENTAVALENT PHOSPHORUS REAGENTS

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Treatment of 2-furanylidenecyanomethyl-1,3-benzothiazole **1** with trialkyl phosphite **2** or dialkyl phosphonate **3** led to the formation of the corresponding-phosphonates **6a,b** *(E&Z)* or **7a,b** *(E&Z)* in high yields (~70%). Only *E*-isomer of both types of phosphonates could be isolated in a pure form. Acrylonitrile **1** reacts with phosphorus ylides **4a,b** to afford the alkylidene derivatives **9a,b** (~58%) along with the pyridone derivative **10** (~38%), meanwhile, with ylide **4c.** The two pyridine derivatives **13a** (41%) and **13b** (54%) were isolated.

Keywords: Acrylonitriles; alkyl phosphites; phosphonates; Wittig reagents

INTRODUCTION

Our continuous interest in the preparation and study of the interaction of the unsaturated nitriles with phosphorus reagents[1–6] prompted us to prepare and examine the reaction of 2-furanylidenecyanomethyl-1,3-benzothiazole **1** with some phosphorus reagents such as trimethyl- and triethyl-phosphites **2a,b** and dimethyl- and diethyl-phosphonates **3a,b** as well as some phosphorus ylides such as alkoxycarbonyl- **4a,b** and formyl-methylenetriphenylphosphoranes **4c.**

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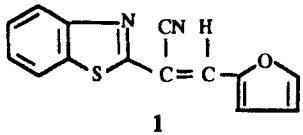


1

$P(OR)_3$

2

$(RO)_2P(O)H$

3

$Ph_3P{=}C(H)COR$

4

2 & 3 a, R = CH_3
b, R = C_2H_5

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

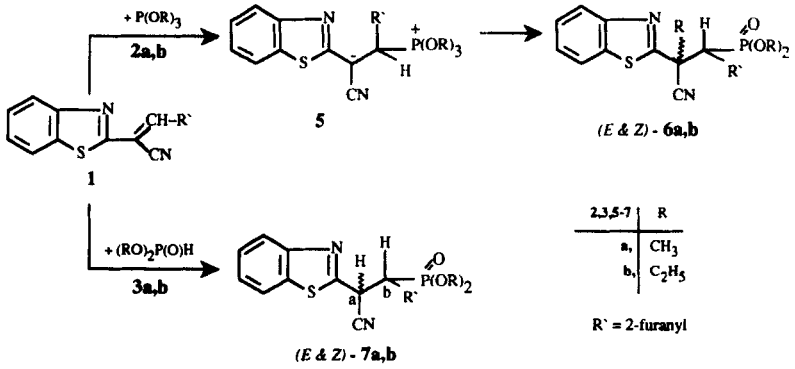
RESULTS AND DISCUSSION

I. Reaction of Acrylonitrile 1 with Trialkyl Phosphites 2a,b

The starting substrate **1** was synthesized by the reaction of equimolar amounts of furanylidenemalonitrile with 2-aminobenzenethiole according to the method previously reported by Saito et al.[7]

The reaction of acrylonitrile **1** and excess of trimethyl phosphite **2a,** employed as a solvent, was completed after heating at 105 °C for ~50 h (TLC) affording the monophosphonate **6a** (71%). It was assigned dimethyl [1(2-furanyl)-2-cyano-2 (1,3-benzothiazol) isopropyl-1-yl] phosphonate **6a** and was found to be a mixture of two resonances at δp 18.12 and 21.42 ppm in its ^{31}P NMR spectrum. These absorptions were assigned to two phosphonate isomers *E*-**6a** and *Z*-**6a** with relative percentages 79% (*E*) and 21% (*Z*), respectively. The suggested *trans*- and *cis*-configurations for the phosphonates *E*-**6a** and *Z*-**6a** are also confirmed from PMR chemical shifts e.g. the ^1H NMR spectrum of **6a** has signals at δ 1.06 (d, C-C**H**$_3$), 4.35 (d, P-C**H**-(2-furanyl) assigned for the major *E*-**6a** as well as δ1.12 (d) and 4.47 ppm (d) assigned-C-C**H**$_3$- and P-C**H**-(2-furanyl) for the minor product *Z*-**6a**.

The higher downfield of the two chemical shifts assigned for the *cis*-isomer is according to the literatures.[8–10] However, the only major isomer *E*-**6a** (44%) was isolated in a pure form by fractional crystallization from acetonitrile. The structural assignment for *E*-**6a** is based upon: (a) its elemental and mass spectral analyses corresponded to an emperical formula $C_{17}H_{17}N_2O_4PS$ (376.4); (b) in the IR spectrum of **6a,** the absorption bands



SCHEME 1

observed at υ 2176, 1463, 1235 and 1074 cm^{-1} were assigned to (CN), (N=C-S),[7] (P=O) and (P-O-CH_3). On the other hand, the band at 1610 cm^{-1} (C=C) present in **1** is absent in the IR spectrum of *E*-**6a**; (c) the ^1H NMR of *E*-**6a** revealed the presence of signals at δ 1.09 (3H, C-C**H**$_3$, d, $^4J_{HP}$=4.2 Hz), the two methoxyl groups attached to the phosphorus atom appeared as two doublets (6H, each with $^3J_{HP}$ = 10.3 Hz) at 3.32 and 3.4 ppm. This splitting is probably due to the asymmetry of the molecule.[11] The exocyclic furanylidene proton (=C**H**-(2-furanyl)) in the PMR of **1** at 8.15 ppm was absent in the spectrum of *E*-**6a**.

Similarly, the reaction of **1** with triethyl phosphite afforded the analogous structure **6b** (*E&Z*) (68%).

A possible mechanism for the formation of compound **6** is depicted in Scheme 1. This is based on initial nucleophilic attack by the phosphite-phosphorus of TAP on the β-carbon atom of α, β-unsaturated nitrile system in **1** to give the C-phosphonium betaine **5**, which undergoes then intramolecular alkyl group translocation (1:2 addition), to afford the phosphonate products **6** (*E* and *Z*).[12,13]

II. Reaction of Acrylonitrile 1 with Dialkyl Phosphonates 3a,b

It has been found that acrylonitrile **1** reacts with dimethyl phosphonate **3a** under the aforementioned conditions with **2** to afford the reaction product

7a which formulated as dimethyl [1 (2-furanyl)-2-cyano-2 (1,3-benzothiazol)-ethyl- 1-yl] phosphonate **7a** (72%).

The ^{31}P NMR spectrum of **7a** showed two resonances at 17.95 (major) and 21.11 ppm (minor) corresponding to two phosphonates *E* and *Z* configurations. The relative percentages were 81% (*E*) and 19% (*Z*), respectively. Only the *trans*-isomer (major) could be obtained in a pure form (*see experimental*).

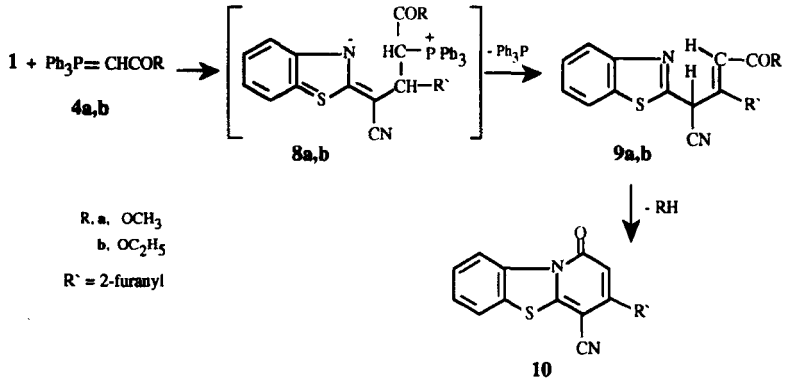
Structure **7a** was postulated for the following reasons: (a) compound **7a** regenerates the starting material **1** upon thermolysis under reduced pressure; (b) elemental analyses and molecular weight determination for **7a** corresponded to $C_{16}H_{15}N_2O_4PS$; (c) its IR spectrum showed absorption bands at 2210 (CN), 1429 (N=C-S), 1230 (P=O) and at 1035 (P-O-CH_3); (d) its ^1H NMR spectrum showed protons of the methoxyl groups attached to phosphorus (6H) as doublet at 4.06 with $J_{HP} = 11.5$ Hz. Each of the exocyclic ethylenic protons (*AB* system) appeared as a doublet of doublets. That of proton **a** (CN-C**H**) was centered at 3.39 with $^3J_{HP} = 11.5$ Hz, while the other proton **b** (P-C**H**) was centered at 3.81 ppm with $^2J_{HP} = 20.5$ Hz.

In the same way acrylonitrile **1** reacts smoothly with diethyl phosphonate to give the phosphonate product **7b.**

III. Reaction of Acrylonitrile 1 with Phosphorus Ylides 4a-c

Next, the behavior of acrylonitrile **1** toward methylene-triphenylphosphoranes **4a-c** has been also studied. Thus, treatment of the substrate **1** with one equivalent of methoxycarbonylmethylenetriphenylphosphorane **4a** in boiling toluene containing triethylamine for ~3 days afforded the corresponding alkylidene adduct **9a** (58%) together with the pyridone **10** (38%). Triphenylphosphine was also isolated and identified. By similar treatment of **1** with ethoxycarbonylmethylenetriphenylphosphorane **4b,** an analogous olefin **9b** (51%) and the same pyridone **10** (29%) were obtained (Scheme 2).

The structures of the isolated products **9a,b** and **10** were in accord with their elemental analyses, molecular weight measurements (MS) and the spectral data. The IR spectrum of the alkylidene **9a** reveals the presence of absorption bands at υ 2211 (CN) and at 1710 cm^{-1} (C=O, ester); δ_H 3.06 (d, 1H, $J_{HH} = 2.1$ Hz, long allyl coupling, -C**H**), 3.71 (s, 3H, OC**H**$_3$), 6.55 – 7.21 (m, 3H, furan-**H**), 7.31 – 7.82 (m, 4H, Ar-**H**); 8.05 ppm (d, 1H,



SCHEME 2

J_{HH} = 2.1 Hz, long allyl coupling, =C**H**); δc 45.1 (-**C**H), 55.1 (O**C**H_3), 110.5 (**C**-CN), 120.1 (C-**C**N), 168.8 (**C**=O), ester).

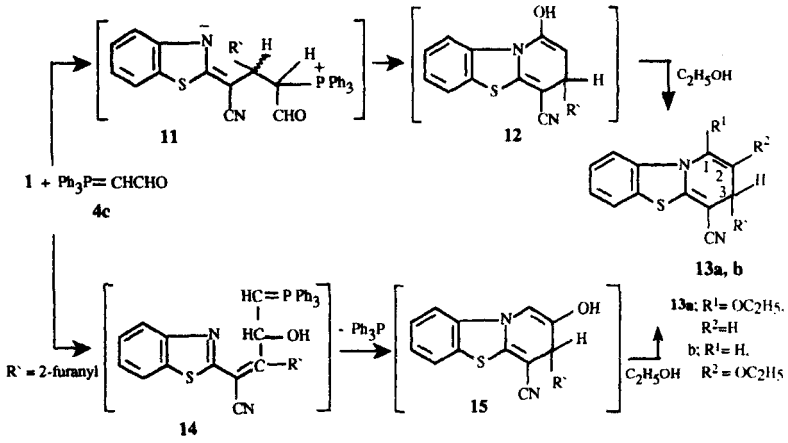
The second product was isolated as light brown crystals and formulated 4-Cyano-1-oxopyrido-3 (2-furanyl) [2,1-*b*][1,3] benzothiazole **10** which confirmed from its elemental analysis and its IR spectrum which revealed the absence of the bands at 1612 and 1427 due to (C=C) and (-N=C-S) and the presence of a band at 1697 cm^{-1} (C=O, amide); the ^1H NMR spectrum showed the absence of the signal at 8.05 ppm for the exocyclic methine proton[7] and appearance of two multiplets in the range 6.5–7.11 and 7.22–7.81 ppm due to the furan and the aromatic protons. The ^{13}C NMR spectrum showed carbon signals at δc 111.2 (**C**-CN), 119.8 (C-**C**N) and at 172.3 ppm (**C**=O, amide),[14]

The formation of **10** is assumed to proceed through an initial attack of the carbanion centre in the Wittig reagent **4a,b** on the active exocyclic electrophilic carbon atom of the acrylonitrile **1** to give a resonance hybrid **8a,b** (Scheme 2) which stabilized by either intra Hofmann elimination of triphenylphosphine to afford **9a,b** or extrusion of a molecule of alcohol and TPP to give the pyridone product **10.**

Conversely, treatment of **1** with formylmethylenetriphenylphosphorane **4c** -prepared *in situ* from its chloride salt in the presence of $NaOC_2H_5$ in ethyl alcohol for 35 h-led to the formation of two pyridine derivatives **13a** (41%) and **13b** (54%).

The structure of **13a** was deduced from correct elemental and spectral data. The NMR exhibited δ_H signals at 1.45 (t, 3H, -C**H**$_3$), 3.52 (d, 1H, J_{HH} = 6.5 Hz, -C**H**), 4.51 (q, 2H, OC**H**$_2$ and at 7.51 – 8.39 ppm (m, 5H, Ar-**H** & pyridine-**H**); δc: 29.1 (**C**H$_3$), 31.5 (-**C**H), 62.6 (O-**C**H$_2$). 110.4 (**C**-CN) and at 121.7 ppm (**C**N).

Although compound **13b** has the same molecular weight it was not identical with structure **13a.** Its ^{1}H NMR showed C-3-H proton as a doublet (J_{HH}=1.9 Hz) at δ 4.1 due to the allylic coupling with the vinyl proton on C-1 which appeared as doublet at δ 6.35.



SCHEME 3

A mechanism proposed for the formation of compounds **13a** and **13b** from the reaction of **1** and **4c** is depicted in Scheme 3, it may be viewed as occurring *via* the attack of **4c** on the furanylidene double bond in two forms (Scheme 3); a) the ylidic form to produce **11,** which by subsequent elimination of triphenylphosphine yields the cyclointermediate **12.** However. O-alkylation process, due to the ethanolic medium,[15] afforded the pyridine derivative **13a.** b) the reduced form of the aldehydic function, by the basic medium and the substrate **1,** to give the intermediate **14,** which is then intramolecularly cyclized with extrusion of triphenylphosphine to afford the pyridine derivative **15** and due to the ethanolic medium compound **13b** was formed. Such reduction of the aldehydic group has been previously documented,[16] and we have invoked it on previous occasion.[15]

EXPERIMENTAL

Melting points are uncorrected, The IR spectra were recorded with a Perkin Elmer spectrophotometer. ^{1}H- and ^{13}C-NMR spectra were recorded in $CDCl_3$ or d_6-DMSO as solvents on a Joel-270 MHz spectrometer, with $SiMe_4$ as an internal standard. The ^{31}P NMR spectra were taken with a Varian CFT-20 (*vs.* – external 85% H_3PO_4). Mass spectra were performed at 70 eV on a Shimadzu GCS-QP 1000 EX spectrometer provided with a data system.

Preparation of 2-Furanylidenecyanomethyl-1,3-benzothiazole 1

2-Furanylidenecyanomethyl-1,3-benzothiazole **1** was prepared according to Saito et al[7] procedure for the preparation of 2-benzylidenecyanomethyl-1,3-benzothiazole as follow: To a mixture of furanylidenemalonitrile[18] (1.44 g, 10 mmol) and 2-aminobenzenethiol (1.25 g, 10 mmol) in ethanol (20 ml), acetic acid (10 mmol) was added, and the mixture was stirred at room temperature for 4 h, and then allowed to stand overnight. The resultant yellow precipitate was isolated by suction and recrystallized from ethanol to give yellow crystals identified as *2-furanylidenecyanomethyl-1,3-benzothiazole* **1** (2.2 g, 87.3%), mp. 128–129°C. Anal. Calcd. for $C_{14}H_8N_2OS$ (252.3): C, 66.65; H, 3.2; N, 11.1; S, 12.71. Found: C, 66.61; H, 3.15; N, 11.03; S, 12.68%. IR (KBr) υ cm^{-1}: 2211 (CN), 1612 (C=C), 1427 (N=C-S). ^{1}H NMR ($CDCl_3$): δ ppm: 6.55–7.5 (3H, furan-**H**, m), 7.65–7.91 (4H, Ar-**H**, m), 8.15 (1H, exocyclic-C**H**,s). MS: m/z = 252 (M^+, 88%).

Reaction of 2-furanylidenecyanomethyl-1,3-benzothiazole 1 with Alkyl Phosphites 2a,b

General Procedure

A mixture of **1** (1.26 g, 5 mmol) and trimethyl phosphite **2a** (5 ml) was heated at 105°C for two days. After evaporation of the volatile materials, *in vacuo,* the residual material was washed twice with cyclohexane to afford the mixture of diastereomers **6a** (*E & Z*) (1.34 g, 71.3%). The proportion of *E*-**6a** : *Z*-**6a** and the ^{1}H NMR data of the isolated mixture were previously described. The mixture of the isomers were redissolved in ace-

tonitrile and kept at –20 °C for 3 days. The solvent was decanted and the procedure was repeated with fresh acetonitrile. The light brown crystals that separated out were collected and proved to be the major isomer *E*-**6a** (820 mg, 43.6%) dec. at 175–177 °C. Anal. Calcd. for: $C_{17}H_{17}N_2O_4PS$ (376.385): C, 54.25; H, 4.55; N, 7.44; P, 8.23; S, 8.52. Found: C, 54.22; H, 4.51; N. 7.4; P, 8.2; S, 8.49%. IR (KBr), υ cm^{-1}: 2176 (CN), 1463 (N=C-S), 1235 (P=O), 1074 (P-O-CH_3). ^1H NMR (d_6-DMSO), δ ppm: δ_H: 1.09 (3H, C-C**H**$_3$, d, $^4J_{HP}$ = 4.2Hz), 3.32 and 3.4 (6H, P-O-C**H**$_3$, 2d, $^3J_{HP}$ = 10.3Hz), 4.37 (1H, P-C**H**, d, J_{HP} = 22.3Hz), 6.55 – 7.41 (3H, furan-**H**, m), 7.58–7.99 (4H, Ar-**H**, m). δ_p = 18.14 ppm. MS: m/z = 376 (M^+, 10%).

Under similar conditions, using the same amounts, Acrylonitrile **1** reacted with triethyl phosphite **2b** and afforded the mixture of diastereomers **6b** (*E&Z*) (1.43 g, 68.4%) which its ^{31}P NMR spectrum showed signals at δ_p = 17.98 and 21.22 ppm which present in ratio 70:30. Also, by fractional crystallization by acetonitrile as mentioned above with **2a,** the major isomer *E*-**6b** was isolated as light brown crystals (841 mg, 40.2%) dec. at 150–152°C. Anal. Calcd. for $C_{20}H_{23}N_2O_4PS$ (418.466): C, 57.4; H, 5.54; N, 6.69; P, 7.4; S, 7.66. Found: C, 57.37; H, 5.5; N, 6.65; P, 7.37; S, 7.63%. IR (KBr) υ cm^{-1}: 2178 (CN), 1228 (P=O), 1052 (P-O-CH_2). ^1H NMR (d_6-DMSO), δ ppm: δ_H: 0.85 (3H, C.CH_2.C**H**$_3$, t), 1.11 (6H, P.O.C.C**H**$_3$, d of t, J_{HH} = 6.5 Hz, J_{HP}= 10.5 Hz), 3.64 (2H, C.C**H**$_2$, qt.), 3.87 (4H, P.O.C**H**$_2$, qt), 4.12 (1H, P.C**H**, d, $^2J_{HP}$= 21.6 Hz), 6.51 – 7.65 (3H, furan – **H**, m), 7.71–8.12 (4H, Ar-**H**, m), δp = 17.99 ppm. MS: m/z = 418 (M^+, 5%).

The minor isomer Z-**6b** could not be isolated in a pure form. Its ^1H NMR (shown in the spectrum of the isomeric mixture) δ_H: 0.99 (3H, C.C.C**H**$_3$, t). 1.23 (6H, P.O.C.C**H**$_3$, m), 3.72 (2H.C.C**H**$_2$, q), 3.99 (4H, P.O.C**H**$_2$, m), 4.21 (1H, P.C**H**, d, $^2J_{HP}$ = 20.8 Hz).

Reaction of Acrylonitrile 1 with Dialkyl Phosphonate 3a,b

General Procedure

A mixture of **1** (1.26 g, 5 mmol) and excess of dimethyl phosphonate **3a** or diethyl phosphonate **3b** (6ml) was heated in absence of solvent for 20 h (TLC). The excess of DAP was removed *in vacuo*, then the residue was washed several times with light petroleum to give a mixture of diastere-

omers **7a** (*E* and *Z*) (1.31 g, 72.4%), ^{31}P NMR: δp = 17.95 and 21.11 ppm (79:21). Working up the reaction mixture **7** in the same manner as described for **6a,b,** yielded the major *E*-**7a** in a pure form and formulated as *Dimethyl [1(2-furanyl)-2-cyano-2 (1,3-benzothiazol) ethyl-1-yl] phosphonate* (*E*-**7a**) (780 mg, 43.1%), mp. 138–140°C (acetonitrile). Anal. Calcd. for $C_{16}H_{15}N_2O_4PS$ (362.358): C, 53.03; H, 4.17; N, 7.73; P, 8.55; S, 8.85. Found: C, 53.01; H, 4.13; N, 7.69; P, 8.53; S, 8.83% IR (KBr) υ cm^{-1}: 2210 (CN), 1429 (N=C-S), 1230 (P=O), 1035 (P.O.C). NMR (d_6-DMSO) δ ppm: δ_H 3.39 (1H, CN-C**H**, d of d, J_{HH} = 6.4 Hz, J_{HP} = 11.5 Hz), 3.81 (1H, P-C**H**, d of d, J_{HH} = 6.4 Hz, J_{HP}= 20.5 Hz), 4.06 (6H, P.O.C**H**$_3$, d, J_{HP}= 11.5 Hz), 6.39–7.41 (3H, furan-**H**, m), 7.6–8.1 (4H, Ar-**H**, m); δp = 17.97 ppm. MS: m/z = 362 (M^+, 23%).

The minor isomer *Z*-**7a** could not be isolated and its signals in the isomeric mixture **7a** at δ_H 3.41 (1H, C**H**-CN, d of d, $^3J_{HP}$ = 10.6 Hz), 3.92 (1H, P-C**H**, d, J_{HP}= 21.5 Hz), 4.18 (6H, P.O.C**H**$_3$, d of d, J_{HP} = 10.6 Hz).

Similarly, the diastereomeric mixture **7b** (1.35 g, 69.2%), ^{31}P NMR: δ_p 17.79 and 20.56 ppm (76:24).

Diethyl [1 (2-furanyl)-2-cyano-2(1,3-benzothiazol) ethyl-1-yl] phosphonate E-**7b** (745 mg, 38.2%) mp. 115–117°C (acetonitrile). Anal. Calcd. for: $C_{18}H_{19}N_2O_4PS$ (390.412): C, 55.38; H, 4.9; N, 7.18; P, 7.93; S, 8.21. Found; C, 55.32; H, 4.81; N, 7.09; P, 7.85; S, 8.15%. IR (KBr) υ cm^{-1}: 2210 (CN), 1439 (N=C-S), 1233 (P=O), 1025 (P.O.C). ^{1}H NMR (d_6-DMSO); δ_H 1.15 (6H, P.O.C.C**H**$_3$, d of t, J_{HP} = 10.5 Hz), 3.38 (1H, C**H**-CN, d of d, $^3J_{HP}$ = 11.5 Hz), 3.81 (1H, P-C**H**, d of d, $^2J_{HP}$ = 21.2 Hz), 4.41 (4H, OC**H**$_2$, d, J_{HP} = 11.5 Hz), 6.45–7.5 (3H, furan-**H**, m), 7.67 – 8.1 (4H, Ar-**H**, m); δp = 17.81 ppm. MS: m/z = 390 (M^+, 12%).

The minor isomer *Z*-**7b** has signals in the isomeric mixture **7b** at δ_H 1.21 (6H, P.O.C.C**H**$_3$), 3.42 (1H, C**H**-CN), 3.86 (1H, P-C**H**), 4.51 (4H, OC**H**$_2$).

All yields based on compound **1.**

Pyrolysis of Adduct 7

Compound **7a** (for example) (0.3 g) was heated in a cold finger sublimator at 150°C (bath temperature) under reduced pressure (5 mm/Hg) for 30 min. The compound that sublimed was collected (161 mg, 77.4%), recrystallized from ethanol to give yellow crystals proved to be 2-furanylidene-cyanomethyl-1,3-benzothiazole **1** (mp. and mixed mps. 128–129°C).

Reaction of Acrylonitrile 1 and Phosphorus Ylides 4a,b

A solution of **1** (1.26 g, 5 mmol) and methoxycarbonylmethylenetriphenylphosphorane **4a**[19] (2.3 g, 7 mmol) in toluene containing triethylamine (0.7 ml) was refluxed for 3 days. The reaction mixture was filtered and the solid product was recrystallized from methylene dichloride to give the alkylidene derivative **9a.**

Compound **9a** was obtained as brown crystals (945 mg, 58.3%) mp. 238–240°C (CH_2Cl_2). Anal. Calcd. for $C_{17}H_{12}N_2O_3S$ (324.365): C, 62.95; H, 3.73; N, 8.64; S, 9.88. Found: C, 62.88; H, 3.65; N, 8.55; S, 9.81%. IR (KBr) υ cm^{-1}: 2211 (CN), 1710 (C=O, ester). NMR ($CDCl_3$), δ_H: 3.06 (1H, long allyl coupling-C**H**, d, J_{HH} = 2.1 Hz), 3.71 (3H, O.C**H**$_3$, s), 6.55–7.21 (3H, furan-**H**, m), 7.31 – 7.82 (4H, Ar-**H**, m), 8.05 ppm (1H, long allyl coupling, =C**H**, d, J_{HH} = 2.1 Hz); δc: 45.1 (-**C**H), 55.1 (O**C**H$_3$), 110.5 (**C**-CN), 120.1 (**C**N), 168.8 ppm (**C**=O, ester). MS: m/z = 324 (M^+, 45%).

After evaporation of the volatile materials from the mother liquour, the remainder was subjected to column chromatography [silica gel-cyclohexane with increasing amounts of chloroform (up to 100%). The first product was triphenylphosphine which isolated and identified.

Fraction up to 8:2 v/v (cyclohexane – chloroform) afforded the pyridone **10** as light brown crystals (559 mg, 38.3%), mp. 160 – 162°C (CH_2Cl_2). Anal. Calcd. for $C_{16}H_8N_2O_2S$ (292.322): C, 65.74; H, 2.76; N, 9.58; S, 10.97. Found: C, 65.69; H, 2.69; N, 9.51; S, 10.92. IR (KBr) υ cm^{-1}: 2210 (CN), 1697 (C=O, amide). NMR ($CDCl_3$), δ_H: 6.5 – 7.11 (3H-furan-**H**, m), 7.22 – 7.81 ppm (5H, Ar-**H** & pyridone **H**, m); δc: 111.2 (**C**-CN), 119.8 (**C**N), 172.3 ppm (**C**=O, amide). MS: m/z = 292 (M^+, 35%).

Similarly, the products **9b** and **10** were obtained upon reacting acrylonitrile **1** with ethoxycarbonylmethylenetriphenylphosphorane **4b** under the same reaction conditions with the same amounts and working up as mentioned above. TPP was also isolated and identified.

Compound **9b** was obtained as brown crystals (862 mg, 51%), mp. 223–225°C (ethanol). Anal. Calcd. for $C_{18}H_{14}N_2O_3S$ (338.392): C, 63.89; H, 4.17; N, 8.28; S, 9.47. Found: C, 63.85; H, 4.1; N, 8.21; S, 9.43%. IR (KBr) υ cm^{-1}: 2205 (CN), 1715 (C=O, ester). ^1H NMR ($CDCl_3$) δ ppm: δ_H 1.38 (3H, O.C.C**H**$_3$, t, J_{HH} = 6 Hz), 3.11 (1H, -C**H**, d, J_{HH} = 2.2 Hz), 3.68 (2H, O.C**H**$_2$, q, J_{HH}= 6 Hz), 6.54 – 7.4 (3H, furan -**H**, m), 7.51 – 7.84 (4H Ar-**H**, m), 8.09 (1H, =C**H**, d, J_{HH} = 2.2 Hz). MS: m/z = 338 (M^+, 5%)

The fraction up to 8:2 v/v gave compound **10** (428 mg, 29.3%).

Reaction of 1 with Phosphorus Ylide 4c

Into a well dried three necked flask containing 0.3 g sodium metal dissolved in 50 ml absolute ethyl alcohol, formylmethylenetriphenylphosphonium chloride[20] (7 mmol) was added portionwise. The reaction mixture was stirred at r.t. for 1 h followed by addition of **1** (1.26 g, 5 mmol) and then heated under reflux for 35 h. The product mixture was concentrated to 20 ml, diluted with 20 ml distd water, acidified with conc. HCl and then extracted with two portions 100 ml $CHCl_3$. The 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 (7:3 → 1:9 v/v) to give compounds **13a** and **13b,** respectively.

4-Cyano-1-ethoxy-3H-3(2-furanyl)-pyrido [2,1-b] [1,3] benzothiazole 13a

Was eluted first as light brown crystals (658 mg, 40.87%), mp. 65 – 67°C (CH_2Cl_2). Anal. Calcd. for $C_{18}H_{14}N_2O_2S$ (322.392): C, 67.06; H, 4.38; N, 8.69; S, 9.95. Found: C, 67.01, H, 4.31; N, 8.62; S, 9.9%. IR (KBr) υ cm^{-1}: 2197 (CN). NMR ($CDCl_3$), δ_H: 1.45 (3H, -C.C**H**$_3$, t), 3.52 (1H, C**H**, d, J_{HH} = 6.5 Hz), 4.51 (2H, OC**H**$_2$, q), 6.5 – 7.39 (3H, furan -**H**, m), 7.51 – 8.39 ppm (5H, Ar-**H** & pyridine -**H**, m); δc: 29.1 (**C**H$_3$), 31.5 (**C**H), 62.6 (O.**C**H$_2$), 110.4 (**C**-CN), 121.7 ppm (**C**N). MS: m/z = 322 (M^+, 20%).

4-Cyano-2-ethoxy-3H-3([2-furanyl)-pyrido [2,1-b][1,3] benzothiazole 13b

Was obtained as brown crystals (875 mg, 54.3%), mp. 110–112°C (ethanol). Anal. Calcd. for $C_{18}H_{14}N_2O_2S$ (322.392): C, 67.06; H, 4.38; N, 8.69; S, 9.95. Found; C, 67.09; H, 4.29; N, 8.61; S, 9.91%. IR (KBr) υ cm^{-1}: 2200 (CN). NMR (d_6-DMSO), δ_H: 1.39 (t, 3H, C**H**$_3$), 4. 1 (1H, C**H**-, d, J_{HH} = 1.9 Hz), 4.48 (q, 2H, OC**H**$_2$), 6.43 – 7.37 (3H, furan-**H**, m), 7.56 –8.19 ppm (4H, Ar-**H**, & N-C**H**, m); δc: 29.1 (**C**H$_3$), 45.6 (**C**-3-H), 62.6 (O-**C**H$_2$), 110.8 (**C**-CN), 120.9 ppm (**C**N). MS: m/z = 322 (M^+, 68%).

Triphenylphosphine was also isolated and identified from this reaction.

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