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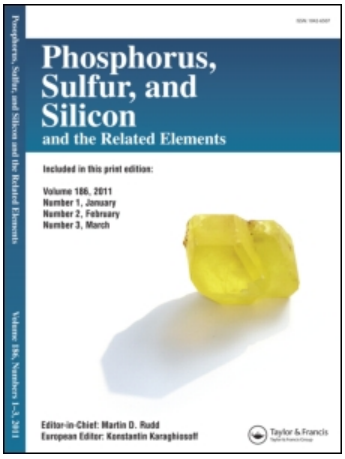

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THE REACTIONS OF ALKYL PHOSPHITES WITH αβ-UNSATURATED CARBON-NITROGEN MULTIPLE-BONDS: 2-BENZYLIDENECYANOMETHYL-1,3-BENZOTHIAZOLE AND α-BENZIL MONOXIME

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THE REACTIONS OF ALKYL PHOSPHITES WITH ∝,β-UNSATURATED CARBON-NITROGEN MULTIPLE-BONDS: 2-BENZYLIDENECYANOMETHYL-1,3-BENZOTHIAZOLE AND ∝-BENZIL MONOXIME

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2-Benzylidenecyanomethyl-1,3-benzothiazole (**1**) reacts with trialkyl phosphites (**6**) to give a mixture of the corresponding-phosphonates **9** (*E* & *Z*) with **6a**,**b** or **16c** (*E* & *Z*) with **6c** (~50%) and -[2,1-*b*]-fused pyrido-derivative **12** (~20%), meanwhile, with dialkyl phosphonates **7** affords only the phosphonates **16** (*E* & *Z*) in high yields (~80%). Only *E*-isomer of both types of phosphonates could be isolated in a pure form. α-Benzil monoxime (**22**) reacts with **6** to give oxazaphospholes **23**, and with **7** to give α-hydroxyamino phosphonates **25**.

Keywords: 1,3-Thiazoles; alkyl phosphites; heterocyclic-phosphonates; 1,3-thiazole-[1,2−*x*]-fused pyrido-compounds; oxazaphospholes; α-hydroxyaminophosphonates

INTRODUCTION

Recently, we investigated reactions of nucleophilic tervalent phosphorus reagents with carbon-nitrogen multiple bonds, e.g., α,β-unsaturated-nitriles [1-5], -monoximes [6], and -anils [7, 8]. The final products obtained depend on the nature of the above reactants.

In a very recent work [9], we have shown that alkoxyphosphonium ylide **2a** attacks the exocyclic benzylidene carbon atom in 2-benzylidenecyanomethyl-

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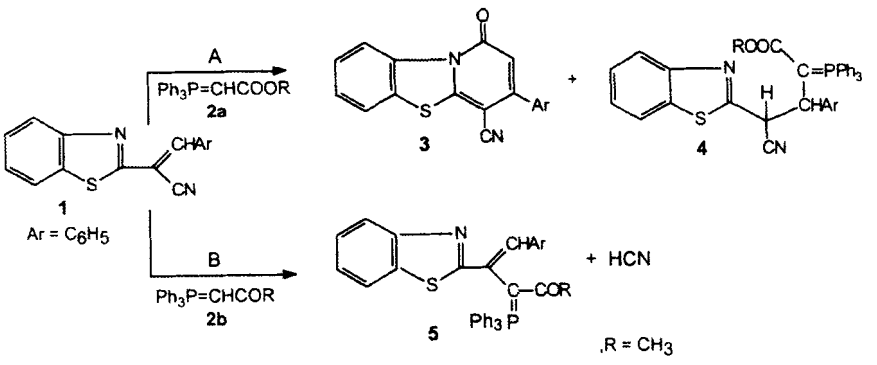

SCHEME 1

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1,3-benzothiazole (**1**) to give the corresponding [1,2-*x*] fused pyridone derivative **3** and the new complex phosphonium ylide **4** (Scheme 1, Pathway A). Conversely, replacement of the nitrile group has occured at the carbanion center in the β-ketoalkylidenephosphorane **2b** to give another type of complex ylide assigned **5** (Pathway B). These results prompted us to study the mode of attack by trialkyl phosphites **6a-c** and dialkyl phosphonates **7a-c** on the α,β-unsaturated system in **1**. The study was extended to the reaction of the same reagents **6** and **7** with α-benzil monoxime.

RESULTS AND DISCUSSION

Reaction of 2-Benzylidenecyanomethyl-1,3-benzothiazole (1) with 6 and 7

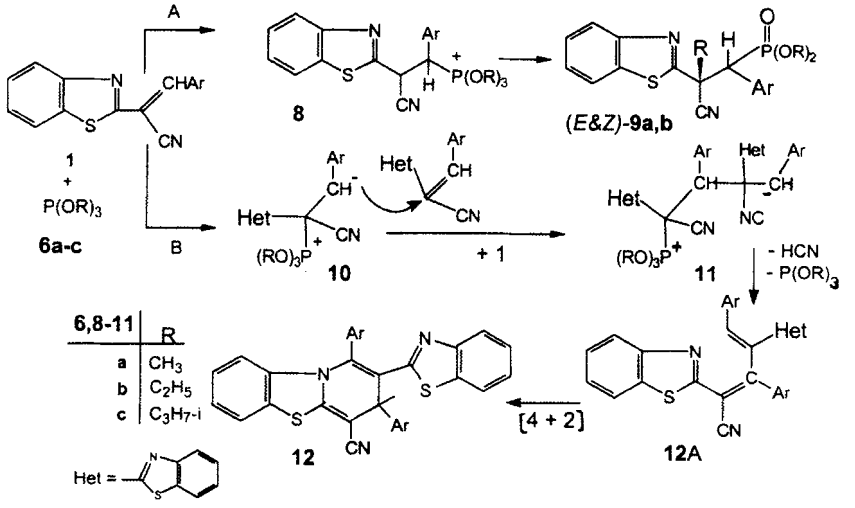
The starting compound **1**, easily accessible from the condensation of 2-cyanomethyl-1,3-benzothiazole with the aromatic aldehydes in ethanol containing few drops of triethylamine according to the method has been described by Saito et al [10].

The reaction of the acrylonitrile **1** with trimethyl phosphite proceeded on heating the reactants at 100°C, in the absence of solvent, for 3 days to give a mixture of two main products (**9a** + **12**) which could be separated by fractional crystallization.

The first yellow crystalline product (43%) assigned dimethyl [1-phenyl-2-cyano-2-(1,3-benzothiazol)isopropyl-1-yl] phosphonate (**9a**) was found to be a mixture of two resonances at δp 18.55 and 21.94 ppm in its ^{31}P NMR spectrum.

These absorptions were assigned to two phosphonate isomers (*E* - **9a** + *Z*-**9a**). The relative percentages were 84% (*E*) and 16% (*Z*), respectively. The suggested *trans*- and *cis*-configurations for the phosphonates *E*-**9a** and *Z* -**9a**, although not established with certainty, are based on the NMR chemical shifts. That the ^{1}H NMR spectrum of this material **9a** has signals at δ 1.95 (d, C-C**H**$_3$), 4.22 (d, P-C**H**-Ar) assigned for the major (*E*-isomer) as well as δ 2.18 (d) and 4.38 (d) assigned to -C-C**H**$_3$- and P-C**H**Ar, respectively, for the minor product (*Z*-isomer). In all cases, the higher downfield of the two chemical shifts observed for the isomer suggested as *cis*-isomer is greater than that of the corresponding isomer, suggested as *trans*, in agreement with the literature [11-13]. However, the only major isomer *E*-**9a** (28%) was isolated in a pure form by fractional crystallization from methylene dichloride .

Compatible elemental analysis and molecular weight determination (MS) for *E*-**9a** corresponded to $C_{19}H_{19}N_2O_3PS$. Its IR spectrum shows strong absorption bands 2184 (CN), 1435 (N=C-S) [10], 1248 (P=O) and at 1028 cm^{-1} (P-O-CH$_3$). Moreover, the strong ethylenic (C=C) band present in the IR spectrum of **1** at 1610 cm^{-1} is absent in the IR spectrum of *E*-**9a**. The ^{1}H NMR of *E*-**9a** spectrum showed protons of the P(O)(OC**H**$_3$)$_2$ group (6H) as a doublet ($^3J_{HP}$ = 10.3 Hz) at δ 3.63. It also showed a doublet (3H, $^4J_{HP}$ = 4.6 Hz) at 1.96. This value is in accordance with the chemical shift expected for a methyl group on an sp^3-carbon



SCHEME 2

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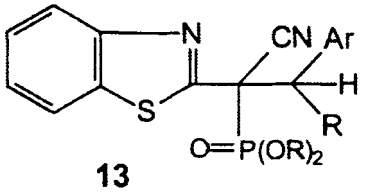

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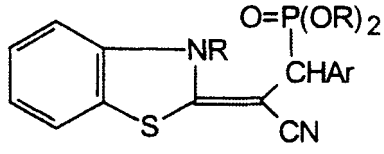

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atom. The exocyclic benzylidene proton (=C**H**Ar) in the PMR of **1** at δ 8.4 ppm was absent in the spectrum of *E*-**9a**, instead, the benzyl methine proton appeared as a doublet at 4.2 ($^2J_{HP}$ = 24.2 Hz). Its ^{31}P NMR spectrum showed a chemical shift, δp = 18.57 ppm. These data recorded for the methyl- and the methine protons in the PMR spectrum of *E*-**9a** as well as the presence of N=C-S absorption band in its IR spectrum can positively confirm the assigned structure **9** and rule out the other possible structures **13** and **14**. Structure **13** would predict a doublet of quartets for the exocyclic benzyl proton and a doublet of doublets resulting for the C**H**$_3$ proton, while structure **14** would predict a singlet for N-methyl protons at $\delta_H \sim 3$ ppm and the presence of an absorption band at ~1620 cm^{-1} in its IR spectrum for the exocyclic conjugation .

The second orange crystalline product (23%) was found to be devoid of phosphorus as is inferred from its elemental analysis and ^{31}P NMR measurements. It is identified as 1,3-diphenyl-2-(1,3-benzothiazol)-4-cyano-3*H*-pyrido[2,1-*b*][1,3]-benzothiazole (**12**) for the following reasons: a) its elemental analysis and molecular weight determination (MS) agreed with the molecular formula $C_{31}H_{19}N_3S_2$; b) the IR spectrum of **12** showed absorption bands at 2195, 2210 (CN), 1426(N=C-S) [10]; c) the ^{1}H NMR spectrum of **12** showed only a singlet at 4.88 (C**H**-Ar) and a multiplets in the range 7.2-8.32 ppm (Ar-**H**).

The reaction products of **1** with **6b** and **6c** are assigned analogous structures **9b** (*E* and *Z*) (55%) and **16c** (*E* and *Z*) (45%), respectively, along with the pyrido-derivative **12** (~20%) on the basis of comparable spectroscopic arguments .

E-**9b** and *E*-**16c** are likewise the only isomers obtained in a pure form. The phosphonate **16c** is unequivocally prepared, from diisopropyl phosphonate **7c** and **1**. This behavior is not unexpected since the bulky isopropyl group would impede the Arbuzove reaction. Instead, partial hydrolysis, (conversion moisture) at the intermediate stage **8c** has occured to give the final product **16c** *via* the intermediate **15** (Scheme 3).

A plausible mechanism that accounts for formation of the observed products **9** and **12** from the reaction of the acrylonitrile **1** and trialkyl phosphites **6** is presented in Scheme 2. This involves an initial nucleophilic attack by the

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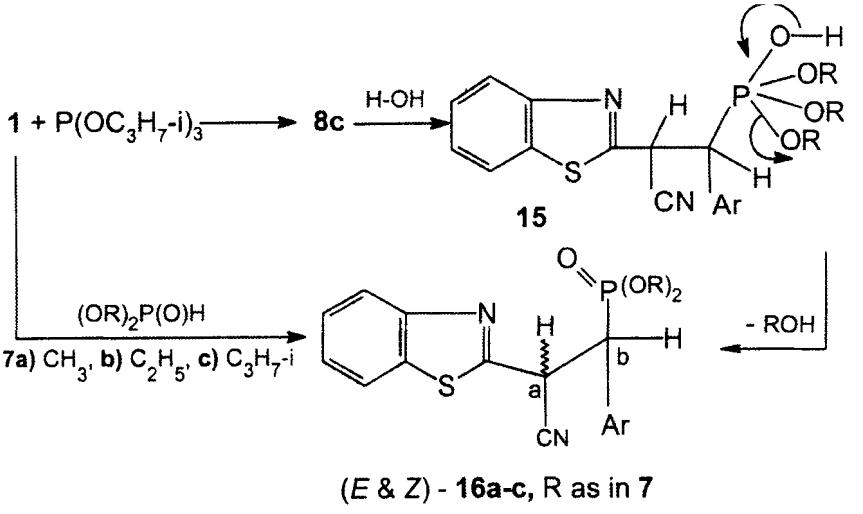

(*E* & *Z*) - **16a-c**, R as in **7**

SCHEME 3

phosphite-phosphorus of TAP on the β-carbon atom of α,β-unsaturated nitrile system in **1** to give the C-phosphonium betaine **8** (Pathway A), which undergoes intramolecular alkyl group translocation (1:2 addition) [1-3], to afford the phosphonate products **9** (*E* and *Z*) with **6a,b** or undergoes partial hydrolysis to give **16c** with **6c**.

Conversely, the formation of the pyridine derivative **12** can be investigated as suggested by a referee, as proceeding through a concurrent attack of PIII on the α-carbon atom with respect to the nitrile group to give the phosphonium intermediate **10** followed by addition of the substrate species **1** to yield the zwitterionic structure **11** (Pathway B). Elimination of HCN and trialkyl phosphite moieties leads to the formation of the pyrido-derivative **12** *via* [4 + 2] cycloaddition of **12A**. An analogous [4 + 2] cycloaddition has already been reported to proceed through an intramolecular cyclization of benzothiazole compounds with extended conjugation [9, 10, 14]. The role of trialkyl phosphites in the formation of **12** has been supported by heating the substrate **1** in toluene at the reflux temperature whereby it is recovered practically unchanged after 4 days. Furthermore, substitution reaction by trialkyl phosphites for the nitrile-group has previously been observed [4, 15].

Next, the behavior of the acrylonitril **1** toward dialkyl phosphonates **7a-c** has been studied (Scheme 3). Treatment of **1** with excess dimethyl phosphonate,

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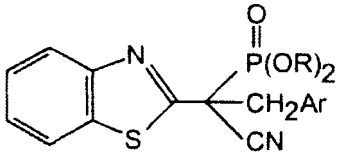
under the conditions previously mentioned with **6**, led to formation of a noncrystalline material assigned dimethyl [1-phenyl-2-cyano-2-(1,3-benzothiazol)-ethyl-1-yl] phosphonate (**16a**) (78%). The pyridine derivative **12** has not been observed in this reaction, meanwhile, the ^{31}P NMR spectrum of **16a** showed two resonances at δ 17.63 (major) and 20.75 ppm (minor) which correspond to two possible phosphonates *E*-and *Z*- configurations. The relative ratio, on the basis of ^{31}P NMR is *E*-**16a**:*Z*-**16b** = 78:22. Only the *trans*-isomer (major) could likewise, be obtained in a pure form.

Structural assignment for structure **16** is based upon correct analytical values and molecular weight determinations (MS) for all new compounds. Adducts **16a-c** regenerate the starting material **1** upon heating above their melting points under reduced pressure. The strong ethylenic (C=C) band present in the IR spectrum of **1** at 1610 cm^{-1}, was absent in the IR-spectra of **16a-c**. However, the IR spectrum of *E*-**16a**, taken as an example, showed the presence of absorption bands at 2215 (CN), 1420 (N=C-S), 1235 (P=O) and at 1050 (P-O-CH_3). Its ^1H NMR spectrum showed the two methoxyl groups attached to the phosphorus atom as a doublet (6H, J_{HP} = 85 Hz) at δ 4.26. The exocyclic ethylenic protons (AB system) appeared as a doublet of doublets. That of proton a (CN-C**H**) was centered at δ 3.32 with $^3J_{HP}$ = 10.8 Hz, while the other proton **b** (P-C**H**) was centered at δ 3.55 ppm with $^2J_{HP}$ = 21.5 Hz. The presence of the *AB* system (-CH-CH-) and the lack of a signal due to the methylene group (-CH_2-P, *cf* **17**) in the PMR spectrum of **16a** or a signal due to N**H** (*cf.* **18**) in its IR or PMR spectra support the assigned structure **16** and rule out either alternative structures such as **17** or **18** .

In summary, from the previous (*see Scheme* 1) [9]-and the present investigations, even though there is a competition between two options available to the penta- and tervalent phosphorus reagents **2,7** and **6** in their reactions with α,β-unsaturated nitrile **1**, i.e. the attack on both carbons of the exocyclic carbon-carbon double bond, it is obvious that the latter reaction is the favorable mode of attack by these reagents. The findings also support the assumption of the tendency of this type of thiazoles to establish the corresponding [2,1-*b*]-fused pyridine-rings [9, 10, 14]. The latter derivatives are of special interest because of



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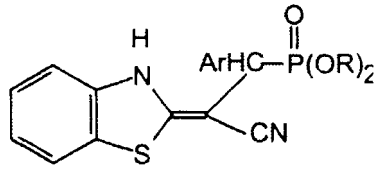

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the numerous uses of these compounds as pesticides [10], especially as herbicides and fungicides [15], disinfictants [16] and a wood preservatives [17].

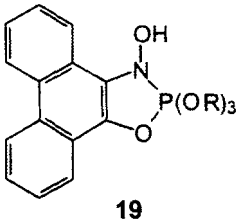
Reaction of α-Benzil Monoxime with TAP and DAP

The reaction of trialkyl phosphites with α-carbonyl-imino compounds (monoximes) takes several interesting courses. For example: trialkyl phosphites and phenanthrene-quinonemonoxime give rise to the formation of the corresponding oxazaphospholes **19** [18], meanwhile, the same reagents react with α-naphthoquinonemonoxime to yield the phosphoramidates **20** [19]. On the other hand, they react with acenaphthenequinone-monoxime by a complex pathway to afford the ketazine **21** [18]. Therefore it seemed of interest to extend the present study to the behavior of the same reagents **6** and **7** with α-benzil-monoxime **22** .

The monoxime **22** was prepared according to the literature [20] and the separation of its stereoisomers were made by recrystallization twice from benzene. The reaction of **22** with TAP (**6**, trimethyl, triethyl, or triisopropyl phosphite), in absence of solvent resulted in the formation of 2,2,2,3-tetrahydro-3- hydroxy -2,2,2- trialkoxydiphenyl-ethylene-(1,2-*d*)-1,3,2- oxazaphospholes (**23**) (~66%).

The oxazaphospholes **23** are pale yellow crystalline substances with sharp melting points and are moderately stable for few weeks at 10°C under dry conditions. Upon thermolysis of **23b**, the oxime substrate **22** was regenerated. The latter result is in agreement with what is known regarding the facile elimination of phosphorus moiety from cyclic compounds [21]. The ^{31}P NMR spectra of **23** show downfield chemical shifts $\delta p = \sim -15$ ppm which are in a good accordance with oxazaphosphole rings [22]. The other NMR spectral data and analysis are consistent with the proposed structure (*see experimental*) .

When benzil monoxime **22** was allowed to react with dimethyl or diethyl phosphonate, yellow crystalline 1:1 adducts were obtained and formulated as



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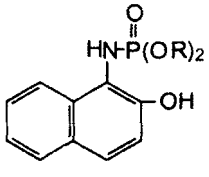

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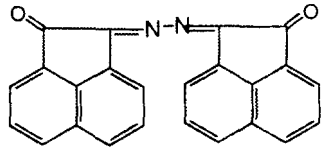

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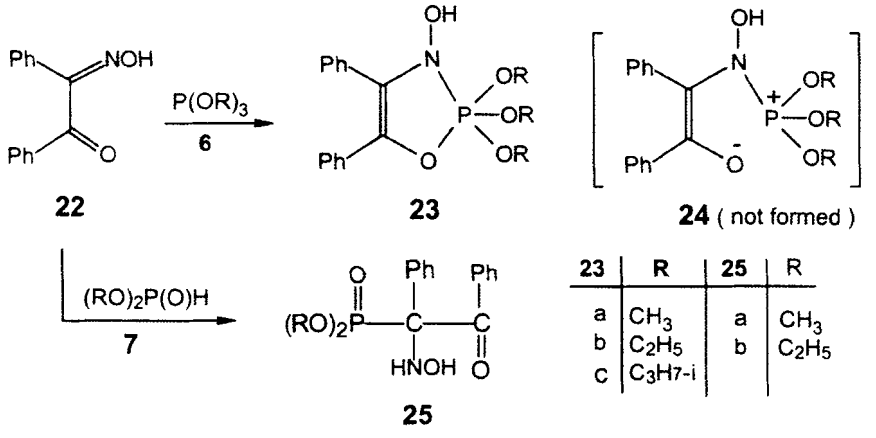

23	R	25	R
a	CH_3	a	CH_3
b	C_2H_5	b	C_2H_5
c	C_3H_{7}-i		

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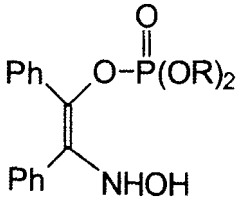
dialkyl (α-hydroxyamino-α-phenacyl) phosphonate (**25a,b**) (Scheme 3) for the following reasons: The ^{31}P NMR shift recorded for compound **25a** was δp= +28.43 ppm. The phosphonate structure in **25** is also established by the presence of a doublet ($^2J_{CP}$ = 87.5 Hz) at δc 59.7 ppm in its ^{13}C NMR spectrum which also showed a signal, among others, at 172.8 ppm (C=O). Moreover, its IR spectrum showed strong absorption bands at 3426 (OH), 3230 (NH), 1670 (C=O), 1235 (P=O) and at 1010 cm^{-1} (P-O-CH_3). Conversely, the strong -C=N- band recorded in the IR spectrum of **22** at 1620 cm^{-1}, was absent in the spectrum of the adduct **25a**. The ^1H NMR spectrum of **25a** revealed that the doublet due to the OCH_3 protons coupled with phosphorus is split into two doublets at δ 3.55 (3H, $^3J_{HP}$ = 10.5 Hz) and at δ 3.62 (3H, $^3J_{HP}$ = 10.5 Hz) due to the asymmetry of the molecule. On the basis of these spectral features, structures like **26-28** can be excluded from further consideration.

From the foregoing observations, it is obvious that α-benzil monoxime reacts with trialkyl phosphites to give oxazaphosphole 1:1 adducts rather than the possible alternative dipolar form (*cf* **24**) as already observed for α-carbonyl-imino compounds. On the other hand, an anomalous behavior, was shown toward dialkyl- phosphonates, whereas a preferential attack at the imino-carbon atom occurs to give 1:1 adducts of type **25**. It is worthy of mention here that imino-carbon attack has previously been observed by these reagents on benzil- and *o*-naphthoquinonemono-anils whereby dialkyl phosphonate adducts **29** and **30** were produced [23], respectively .



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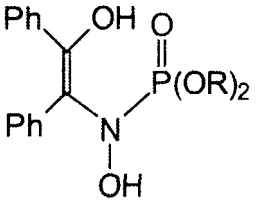

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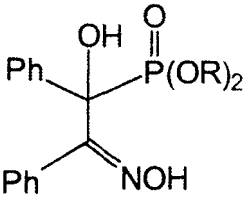

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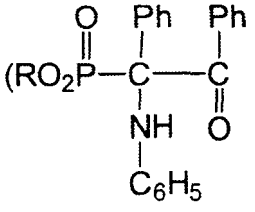
EXPERIMENTAL

All melting points were uncorrected. The IR spectra were obtained with a Philips Infracord Spectrometer Model PU 9712 in KBr discs. The ^1H NMR spectra were recorded in $CDCl_3$ or d_6-DMSO as solvents on a Joel-270 MHz Spectrometer 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). Mass spectra were performed at 70 eV on a Shimadzu GCS-QP 1000 EX Spectrometer provided with a data system. The appropriate precautions in handling moisture-sensitive compounds were observed. Solvents were dried by standard techniques. Compound 1 was prepared as previously reported [10].

Reaction of 2-Benzylidenecyanomethyl-1,3-benzothiazole (**1**) *with Trialkyl Phosphites* (**6a-c**). *A. With trimethyl phosphite: General Procedure*

A mixture of **1** (1 g, 0.38 mol) and trimethyl phosphite (**6a**) (5 ml) was heated at 100-105°C for 3 days. Excess of phosphite was distilled off, *in vacuo*, and the



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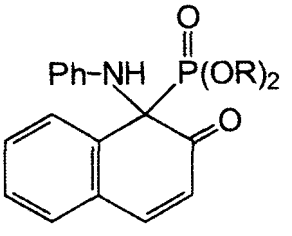

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residue was triturated first with light petroleum (b.r. 40-60°C) and then recrystallized twice from methanol-benzene (1:2) to give bright orange microcrystals of 1,3-diphenyl-2-(1,3-benzothiazol)-4-cyano-3*H*-pyrido[2,1-*b*] [1,3]-benzothiazole (**12**) (200 mg, 23.3%), m.p. 198-200°C. Anal. Calcd. for $C_{31}H_{19}N_3S_2$ (497.65): C, 74.82; H, 3.85; N, 8.44; S, 12.88. Found: C, 74.77; H, 3.81; N, 8.37; S, 12.83%. IR (KBr) υcm^{-1}: 2195, 2210 2210 (CN), 1426 (N=C-S). ^{1}H NMR (d_6-DMSO): δ ppm: 4.88 (s, 1H, C**H** Ar), 7.2-8.32 ppm (m, 18H, Ar.**H**). MS: m/z = 497 (M^+, 11%).

The volatile materials were evaporated from the benzene-methanol filtrate, *in vacuo*, and the oily residue afforded the mixture of diastereomers **9a** (*E* & *Z*) (640 mg, 43.6%). The proportion of *E*-**9a**:*Z*-**9a** and the ^{1}H NMR data of the isolated mixture were previously described. The mixture of the isomers were redisolved in CH_2Cl_2 and kept at −20°C for 2 days. The solvent was decanted and the procedure was repeated with fresh CH_2Cl_2. Crystals that separated out were collected and proved to be the major isomer *E*-**9a** (422 mg, 28.7%) mp. 85-87°C. Anal Calcd. for: $C_{19}H_{19}N_2O_3PS$ (386.42): C, 59.05; H, 4.95; N, 7.25; P, 8.02; S, 8.3. Found: C, 59.63; H, 4.87; N, 7.18; P, 8.1; S, 8.24%. IR (KBr), υ cm^{-1}: 2184 (CN), 1435 (N=C-S), 1248 (P=O), 1028 (P-O-CH_3). ^{1}H NMR ($CDCl_3$), δ ppm: δ_H 1.96 (3H, C - C**H**$_3$, d, $^4J_{HP}$ = 4.5Hz), 3.63 (6H, P-O-C**H**$_3$, $^3J_{HP}$ = 10.3 Hz), 4.2 (1H, P - C**H**, d, $^2J_{HP}$ = 24.2 Hz), 7.43-8.03 (9H, Ar-**H**, m); δ_P=18.57 ppm. MS: m/z = 386 (M^+, 35%).

With Triethyl Phosphite

Similarly **12** (18.7%) and **9b** (*E* and *Z*) (55.2%) were obtained upon reacting compound **1** with triethyl phosphite (**6b**) at 100°C in the absence of solvent for 3 days, similar to the general procedure, using the same amounts. The mixture of diastereomers **9b** is tested first by ^{31}P and ^{1}H NMR spectra whereby they present in ratio 3:1 in its ^{31}P NMR spectrum at δp = 18.21 and 21.33 ppm. Likewise with **9a**, fractional crystallization from CH_2Cl_2 afforded a pure sample of the major isomer *E*-**9b** as yellow crystals (480 mg, 30%, based on the starting material), m.p. 72-74°C. Anal Calcd. for $C_{22}H_{25}N_2O_3PS$ (428.5): C, 61.66; H, 5.88, N, 6.54; P, 7.23; S, 7.48. Found: C, 61.71; H, 5.83; N, 6.43; P, 7.12; S, 7.4%. IR (KBr) ν cm^{-1}: 2188 (CN), 1255 (P=O), 1020 (P-O-CH_2). ^{1}H NMR ($CDCl_3$), δ ppm: δ_H: 0.97 (3H, C.CH_2C**H**$_3$, t, J_{HH} = 6.5 Hz), 1.28 (6H, POC.C**H**$_3$, d of t, J_{HH} = 6.8 Hz), 3.75 (2H, C.C**H**$_2$, qt.), 4.06 (4H, P-OC**H**$_2$, qt, J_{HP} = 11.3 Hz), 4.21 (1H. P-CH, d, $^2J_{HP}$ = 22.7 Hz), 71.8-8 (9H, Ar-**H**, m), δp = 18.22 ppm. MS: m/z = 428 (M^+, 22%).

The minor isomer *Z*-**9b** could not be isolated in a pure form. Its ^{1}H NMR (shown in the spectrum of the isomeric mixture) δ_H 1.12 (3H, C.C.C**H**$_3$, t), 1.35

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(6H, P.O.C.CH_3, t), 3.97 (2H, C.CH_2, q), 4.11 (4H, P-O-CH_2, qt), 4.3 (1H, P-CH, d, $^2J_{HP}$ = 22.5 Hz).

With Triisopropyl Phosphite (**6c**)

Acrylonitrile **1** reacts with **6c** whereas the procedure and working up are the same (with **6a,b**) using the same amounts. The product residue after removing the excess of the phosphite was treated as mentioned before. The CH_2Cl_2-insoluble material of **12** was recrystallized from methanol-benzene (1:2) (177 mg, 20%) (mps. and comparative spectra).

The CH_2Cl_2 solution obtained above was evaporated to give the mixture of diastereomers **16c** (^{31}P NMR: δ 17.4 (*E*) and 20.02 ppm (*Z*) the ratio is *E*:*Z* = 72:28%. Likewise with **9a, b**, fractional crysallization from CH_2Cl_2 yielded a pure sample of the major isomer *E*-**16c** as yellow crystals (416 mg, 26%), m.p. 80-82°C. Anal Calcd. for $C_{22}H_{25}N_2O_3PS$ (428.5): C, 61.66; H, 5.88; N, 6.54; P, 7.23; S, 7.48. Found : C, 62.58; H, 5.79; N, 6.47; P, 7.32; S, 7.44%. IR (KBr) υcm^{-1}: 2184 (CN), 1252 (P=O), 1005 (P-O-C). ^{1}H NMR ($CDCl_3$), δ ppm δ_H: 0.75 (12H, O.CH(CH_3)$_2$, d, J_{HH} = 6.8 Hz), 3.54 (1H, C.CH, d, J_{HH} = 8.2 Hz), 3.78 (2H, OCH.C, sept., $^3J_{HP}$ = 13.2 Hz), 4.17(1H, P-CH, d, $^2J_{HP}$ = 21.8 Hz), 7.2-8.17 (9H, Ar-H, m), δp = 17.48 ppm. MS: m/z = 428 (M^+, 33%).

The minor isomer *Z*-**16c** could not be isolated in a pure form. Its ^{1}H NMR (shown in the spectrum of the isomeric mixture), δ_H: 0.82 (12H, OCH-CH_3, d, J_{HH} = 6.8 Hz), 3.64 (1H, C.CH, d), 3.88 (2H, OCH.C, sept.), 4.24 (1H, P-CH, d, $^2J_{HP}$ = 21.6 Hz).

No conversion for substrate **1** to **12** was observed, however, in a parallel experiment when compound **1** was refluxed in toluene after 4 days.

Reaction of **1** *with Dialkyl Phosphonates* (**7a-c**)

A mixture of the acrylonitrile **1** (1 g, 0.38 mol) and excess of dimethyl, diethyl and diisopropyl-phosphonate (6 ml) was heated at 100°C in absence of solvent for 3 days (TLC). Excess of DAP was distilled off to give a mixture of diastereomers **16** (*E* and *Z*) as yellow substances. Working up the reaction mixture **16** in the same way as described for **9a, b**, resulted in isolation of *E*-**16a-c** in a pure form.

The diastereomeric mixture **16a** (1.16 g, 82.3%), ^{31}P NMR : δp 17.63 and 20.75 ppm (78:22).

*Dimethyl [1-phenyl-2-cyano-2-(1,3-benzothiazol)ethyl-1-yl] phosphonate (E-***16a**) (0.6 g, 44%, based on **1**), m.p. 103-105°C (CH_2Cl_2). Anal. Calcd. for $C_{18}H_{17}N_2O_3PS$ (372.4) : C, 58.05; H, 4.6; N, 7.52; P, 8.32; S, 8.61. Found : C,

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58.13; H, 4.54; N, 7.49; P, 8.43; S, 8.53%. IR(KBr) υ cm^{-1}: 2215 (CN), 1420 (N=C-S), 1235 (P=O), 1050 (P-O-C). NMR($CDCl_3$) δppm : δ_H 3.32 (1H, C**H**-CN, d of d, $^3J_{HP}$ = 10.8 Hz), 3.55(1H, P-C**H**, d of d, $^2J_{HP}$ = 21.5 Hz), 4.26 (6H, O**CH$_3$**, d, J_{HP} = 10.8 Hz), 7.28-7.86 (9H, Ar-**H**, m), δ_P=17.65 ppm. MS: m/z = 372 (M^+, 42%).

The minor isomer Z-**16a** could not be isolated in a pure form. Its ^1H NMR (shown in the spectrum of the isomeric mixture); δ_H 3.39 (1H, C**H**-CN, d of d, $^3J_{HP}$ = 10.8 Hz), 3.7 (1H, P-C**H**), 4.31(6H, O**CH$_3$**).

The diastereomeric mixture **16b** (1.15 g, 75.5%), ^{31}P NMR : δ 17.83 and 20.23 ppm (70:30).

Diethyl [1-phenyl-2-cyano-2(1,3-benzothiazol) ethyl-1-yl] phosphonate (*E*-**16b**) (568 mg, 37.2%, based on **1**), m.p. 92-94°C (CH_2Cl_2). Anal. Calcd. for: $C_{20}H_{21}N_2O_3PS$ (400.45): C, 59.99; H, 5.29; N, 6.99; P, 7.74; S, 8.0. Found: C, 59.88; H, 5.23; N, 6.9; P, 7.86; S, 7.73%. IR(KBr) υ cm^{-1}: 2210 (CN), 1425 (N=C-S), 1233 (P=O), 1010 (P-O-CH_2). ^1H NMR($CDCl_3$) δppm: δ_H 1.06 (6H, POC.C**H$_3$**, d of t, J_{HH} = 6.8 Hz), 3.23 (1H, C**H**-CN, d of d, $^3J_{HP}$ = 11.2 Hz), 3.48 (1H, P-C**H**, d of d, $^2J_{HP}$ = 21.09 Hz), 4.21 (4H, O**CH$_2$**, d, J_{HP} = 11.2 Hz), 7.25-7.88 (9H, Ar-**H**, m); δp = 17.86 ppm. MS: m/z = 400 (M^+, 50%).

The minor isomer Z-**16b** has signals in the isomeric mixture **16b** at δ_H 1.12 (6H, POC.C**H$_3$**), 3.28 (1H, C**H**-CN), 3.52(1H, P-C**H**), 4.35(4H, O**CH$_2$**).

The diastereomeric mixture **16c** (1.16 g, 72.3%) has the same ^{31}P NMR signals and the same percentages as previously described with the product of **6c**.

Diisopropyl [1-phenyl-2-cyano-2-(1,3-benzothiazol) ethyl-1-yl] phosphonate (*E*-**16c**) was also isolated in a pure form (768 mg, 48%), m.p. and mixed m.ps. and comarative IR and mass spectra with that previously obtained.

Thermal Decomposition of the Adduct **16**

Adduct **16a**, taken as an example, (0.3 g) was heated in a cold-finger sublimator at 120°C (bath temperature) under reduced pressure (1mm/Hg) for about 20 minutes. After cooling, the residual substance was recrystallized from ethanol to give pale yellow crystals proved to be 2-benzylidenecyanomethyl-1,3-benzothiazole (1) (m.p. and mixed m.ps. 121-123°C, yield: 0.27 g, 90%).

Reaction of α-Benzil-monoxime (**22**) *with Trialkyl phosphites* (**6a-c**)

General Procedure. A mixture of the oxime **22** [20] (1 g, 4 mmol) and trimethyl, triethyl or triisopropyl phosphite (5 ml) was heated at 100°C for ~30 h (TLC). After evaporation of the volatile materials, *in vacuo*, the residual substance so obtained, was recrystallized from the appropriate solvent to give the expected oxazaphospholes **23a-c**.

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2,2,2,3-Tetrahydro-3-hydroxy-2,2,2-trimethoxydiphenylethylene-(1,2-d)-1,3,2-oxazaphosphole (**23a**) was obtained as pale yellow crystals (~1 g, 63%), m.p. 106-107°C (acetonitrile). Anal. Calcd. for $C_{17}H_{20}NO_5P$ (349.33): C, 58.45; H, 5.77; N, 4.01; P, 8.87. Found. C, 58.52; H, 5.71; N, 3.93; P, 8.75 %. IR (KBr) νcm^{-1}: 3420 (OH), 1070 (P-O-CH_3). ^1H NMR δ ppm: 3.48 (9H, OC**H**$_3$, d, $^3J_{HP}$ = 12 Hz), 7.2-7.8 (10H, Ar-**H**, m), 8.15 (1H, N-O**H**, d). δp = −15.8 ppm. MS: m/z = 349 (M^+, 100%).

2,2,2,3-Tetrahydro-3-hydroxy-2,2,2-triethoxydiphenylethylene-(1,2-d)-1,3,2 oxazaphosphole (**23b**) was obtained as pale yellow crystals (~1.2 g, 68%), m.p. 93-95°C (hexane). Anal. Calcd. for $C_{20}H_{26}NO_5P$ (391.42): C, 61.37; H, 6.69; N, 3.58, P, 7.91. Found: C, 61.28, H, 6.6; N, 3.46; P, 8.03%. IR (KBr) νcm^{-1}: 3425 (OH), 1038 (P-O-CH_2). ^1H NMR, δ ppm: 0.96 (9H, O.C.C**H**$_3$, t, J_{HH} = 6.6 Hz), 3.85 (6H, OC**H**$_2$, qnt, J_{HH} = 6.6 Hz), 7.25-7.8 (10H, Ar-**H**, m), 8.15 (1H, N.O**H**, d). δp = −14.6 ppm. MS: m/z = 391 (M^+, 100%).

The yellow crystals of adduct **23c** were obtained (~1g, 56%) from CH_2Cl_2-pentane), m.p. 110-112°C. Anal. Calcd. for $C_{23}H_{32}NO_5P$ (433.5): C, 63.72; H, 7.44; N, 3.23; P, 7.15. Found: C, 63.8; H, 7.37; N, 3.15; P, 7.24%. IR (KBr) νcm^{-1}: 3410 (OH), 1015 (P-O-C). ^1H NMR, δ ppm: 1.15 (18H, O.C.C**H**$_3$, d, J_{HH} = 6.5 Hz), 3.48 (3H, P-O-C**H**, sept.), 6.8-7.5 (10H, Ar-**H**, m), 7.8 (1H, N-O**H**, d). δp = −14.22 ppm. MS: m/z = 433 (M^+, 33%).

Reaction of α-benzil-monoxime (22) with Dialkyl phosphonates (**7a,b**).

General Procedure: A mixture of compound **22** (1 g, 4 mmol) and DAP (7, dimethyl or diethyl phosphonate) (5 ml) was heated at 100°C for 30 h. After evaporation of the volatile materials, *in vacuo*, the residual substance was recrystallized from the appropriate solvent to give **25a** or **25b**, respectively.

Dimethyl (α-hydroxyamino-α-phenacyl) phosphonate (**25a**) was obtained as yellow crystals (~1 g, 72%). m.p. 88-89°C (cyclohexane). Anal Calcd. for $C_{16}H_{18}NO_5P$ (335.5): C, 57.31; H, 5.41; N, 4.18; P, 9.24. Found: C, 57.42; H, 5.37; N, 4.11; P, 9.3%. IR (KBr) νcm^{-1}: 3426 (OH), 3230 (NH), 1670 (C=O), 1235 (P=O), 1010 (P-O-C). ^1H NMR, δ ppm 3.55, 3.62 (6H, O.C**H**$_3$, 2d, $^3J_{HP}$ = 10.5 Hz), 7.25-7.85 (10H, Ar-**H**, m), 8.38 (1H, O**H**, s), 11.2 (1H, N**H**, br.). δc: 54.6, 55.2 (2d, OCH_3), 59.7 (d, ^2Jcp = 87.5 Hz, **C**-P), 172.8 (**C**=O). δp = 28.4 ppm. MS: m/z = 335 (M^+, 100%).

Diethyl (α-hydroxyamino-α-phenacyl) phosphonate (**25b**) was obtained as yellow crystals (1.2 g, 75%, m.p. 81-82°C (diethyl ether-cyclohexane, 1:2 v/v). Anal. Calcd. for $C_{18}H_{22}NO_5P$ (363.36): C, 59.5; H, 6.1; N, 3.85; P, 8.53. Found: C, 59.42; H, 6.04; N, 3.7; P, 8.59%. IR (KBr) νcm^{-1}: 3425 (OH), 3380 (NH), 1672 (C=O), 1235 (P=O); 1030 (P-O-C). ^1H NMR, δ ppm: 1.25, 1.35 (6H,

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C.C**H**$_3$, 2t, J_{HH} = 6.2 Hz) 3.85, 4.05 (4H, OC**H**$_2$, 2 qnt, J_{HH} = 6.2 Hz), 7.15-7.8 (10H, Ar-**H**, m), 8.2 (1H, O**H**, br.), 10.5 (1H, N**H**, br.). δp = 29.29 ppm. MS: m/z = 363 (M^+, 100%).

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