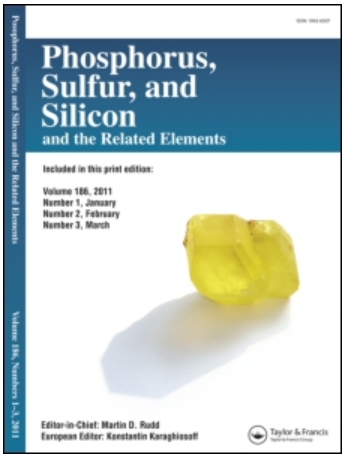

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Preparation of 1,4-Benzothiazines Using Stable Phosphorus Ylides

Mohammad Reza Islami[a]; Said Gharib-Hosseini[a]; Hamid Reza Bijanzadeh[b]
[a] Department of Chemistry, Shahid ahonar University of Kerman, Kerman, Iran [b] Department of Chemistry, Tarbiat Modarres University, Tehran, Iran

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Preparation of 1,4-Benzothiazines Using Stable Phosphorus Ylides

Mohammad Reza Islami
Said Gharib-Hosseini
Department of Chemistry, Shahid Bahonar University of Kerman, Kerman, Iran

Hamid Reza Bijanzadeh
Department of Chemistry, Tarbiat Modarres University, Tehran, Iran

Heating of stable phosphorus ylides in boiling dioxane as a solvent results in ring closure with extrusion alcohol and triphenyphosphine and to give alkyl-2-(3-oxo-3,4-dihydro-2H-1,4-benzothiazin-2-yliden)acetates in good to excellent yields.

Keywords 1,4-Benzothiazines; stable phosphorus ylides; triphenylphosphine

INTRODUCTION

Some time ago, a synthetic method for the preparation of stable phosphorus ylides from the reaction of electron-deficient acetylenic compounds with NH, SH, and CH-acids in the presence of a desired phosphine was described.[1–8] An example of this synthesis is found in the work of Esmaili and our research group.[9] They have reported that the isolated products **4** were obtained in excellent yields from the reaction mixture of dialkyl acetylenedicarboxylate and 2-aminothiophenol in the presence of triphenylphosphine (Scheme 1).

Recently, Yavari and co-workers[10] have reported a new approach for the synthesis of aryliminophosphoranes by heating of phosphorus ylides in boiling *p*-xylene.[10] However, this protocol is limited to α-aminophosphorus ylides. In our efforts toward the preparation of heterocyclic compounds such as 1,4-benzothiazine derivatives 5 containing

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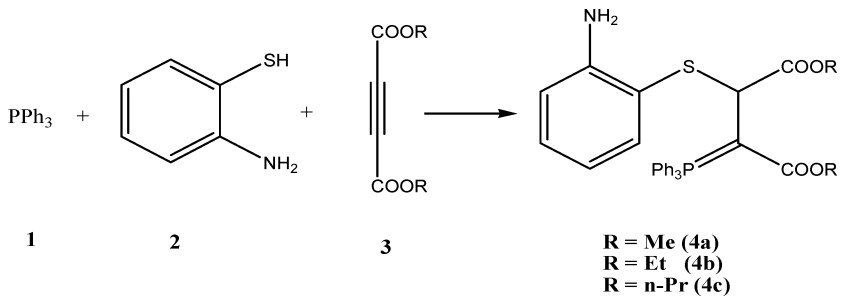
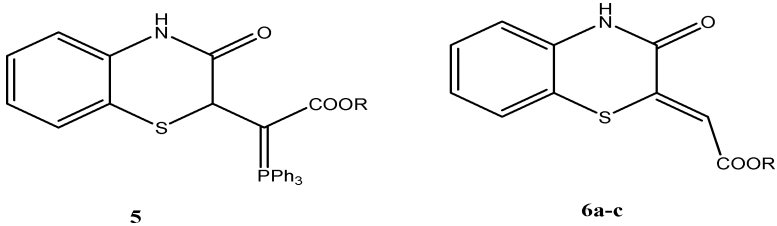
Address correspondence to Mohammad Reza Islami, Department of Chemistry, Shahid Bahonar University of Kerman, P.O. Box 76169-133, Kerman, Iran. E-mail: mrislami@mail.uk.ac.ir



SCHEME 1

ylide moiety, the alkyl 2-[(2-aminophenyl)sufanyl]-3-(1,1,1-triphenyl–λ^5-phosphoranylidene) succinate **4** was heated in boiling dioxane. Although, compound **5** was not observed but 1,4-benzothiazine derivatives **6** were isolated from the reaction mixture. Since the synthetic application of benzothiazine derivatives has increased enormously in medicinal chemistry,[11–13] herein we report the results of this investigation.



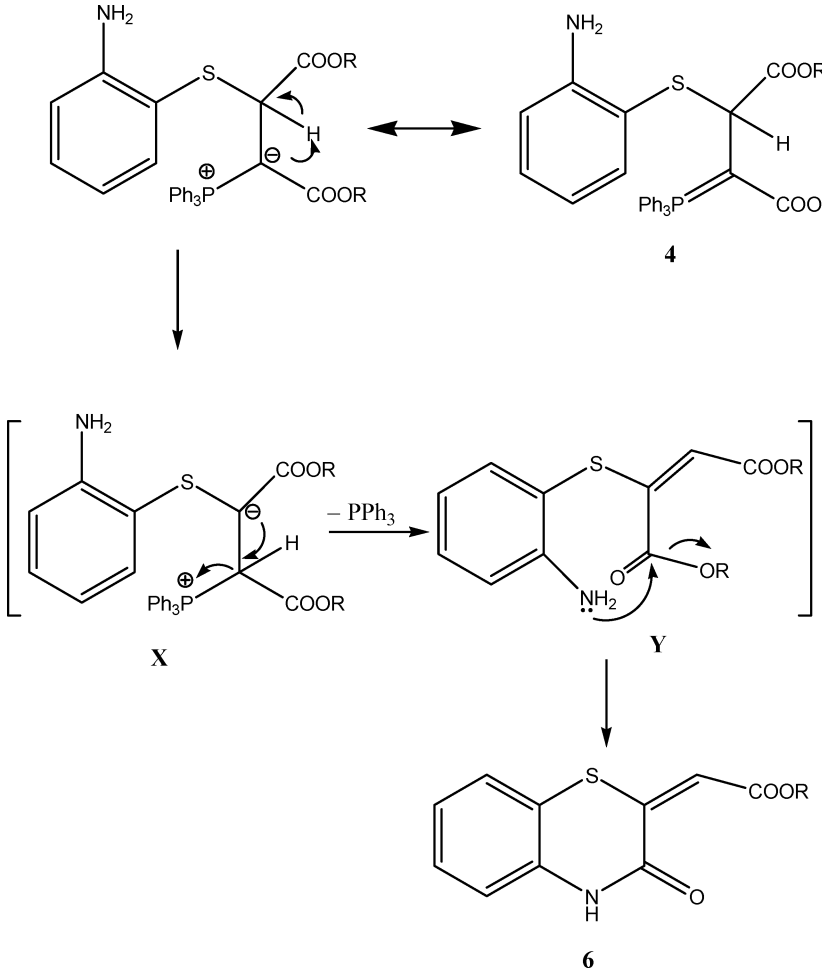
5 **6a-c**

RESULTS AND DISCUSSION

The structures of compounds **6a–c** were deduced from their IR, ^{1}H NMR, and ^{13}C NMR spectra. In the ^{1}H NMR spectrum of **6a**, the signal due to the methoxy group was observed at δ 3.71 ppm as a singlet and the NH proton resonated as a fairly broad signal at δ 11.51 ppm (exchangeable by D_2O). The vinyl CH proton appeared at δ 6.89 ppm as a singlet. The aromatic protons appeared as a multiplet at δ 7.04–7.39 ppm. The ^{13}C NMR spectrum of compound **6a** showed eleven distinct resonances in agreement with the 1,4-benzothiazine structure. The two carbonyl groups along with the methoxy group were observed at δ 165.81, 154.12, and 51.64 ppm, respectively. Other signals, due to aromatic rings and the vinyl moiety, appeared as characteristic resonance lines with the corresponding chemical shifts (see Experimental

section). The ^{1}H NMR and ^{13}C NMR spectra of heterocyclic compounds **6b–c** are similar to those of **6a**, except for signals from the ester group which appear as characteristic resonance lines with the corresponding chemical shifts. The structural assignments made for compounds **6a–c** on the basis of the ^{1}H and ^{13}C NMR spectra were also supported by their IR spectra. The carbonyl region of the spectra exhibits one distinct IR absorption band for each compound.

Although we have not established a mechanism for the formation of compounds **6a–c** in an experimental manner, a reasonable possibility is indicated in Scheme 2.



SCHEME 2

In this mechanism, it is assumed that compound **4** undergoes a [1, 2] proton shift and then leads to intermediate **X**. This 1,3-dipolar intermediate is thermally unstable and rapidly converts to intermediate **Y**. The formation of alkyl-2(3-oxo-3,4-dihydro-2H-1,4-benzothiazin-2-yliden) acetates from intermediate **Y** in the final step of this mechanism can be considered as a product of a lactamization reaction.

In conclusion, heating of stable phosphorus ylides containing β-aminothiophenol in dioxane as a solvent provides a convenient preparative process to 1,4-benzothiazines. These ylides may be considered as new precursors in the synthesis of useful organic compounds such as bezothiazine derivatives.

EXPERIMENTAL

Melting points were recorded on a Gallenkamp melting point apparatus and are uncorrected.NMR spectra were recorded at 500 (^{1}H) and 125.77 (^{13}C) MHz on BRUKER DRX-500 AVANCE spectrometer at 500 and 125.77 MHz, respectively. Chemical shifts are reported (δ) relative to TMS (^{1}H) and $CDCl_3$ (^{13}C) as the internal standards. IR spectra were measured on a Mattson 1000 FT-IR spectrophotometer. Stable phosphorus ylides **4a–c** were prepared according to the reported procedure in the literature.[9]

Methyl-2-(3-oxo-3,4-dihydro-2*H*-1,4-benzothiazin-2-yliden)acetate(6a)

The suspension of methyl 2-[(2-aminophenyl)sufanyl]-3-(1,1,1-triphenyl–λ^5-phosphoranylidene) succinate **4a** (1 g, 2 mmol) in dioxane (20 mL) was heated under reflux for 4 h. The resulting solid was then filtered off, and crystallized from ethanol. The product was filtered and dried to yield **6a**. The product **6a** was obtained as a yellow powder, m.p. 235–237°C decomposed, 0.42 g yield 89%. IR (KBr) ($\nu_{max,}$ cm^{-1}): 3196 (NH), 1681 (C=O), 1609 (C=C). ^{1}H NMR: δ 3.71 (3H, s, OCH_3) 6.89(1H, s, vinyl proton), 7.04–7.39 (4H, m, arom), 11.51 (1H, br.s, NH). ^{13}C NMR: δ 51.64 (OCH_3), 113.67 (=CH) 114.95 (C), 117.02, 123.35, 125.13 and 127.15 (4CH), 132.67 and 140.97 (2C),154.12 and 165.81 (2C=O).

Ethyl-2-(3-oxo-3,4-dihydro-2*H*-1,4-benzothiazin-2-yliden)acetate (6b)

Yellow powder, m.p. 208–211°C decomposed, 0.45 g, yield 90%. IR (KBr) ($\nu_{max,}$ cm^{-1}): 3280 (NH), 1691 (C=O), 1600 (C=C). ^{1}H NMR: δ 1.23 (3H, t, $^3J_{HH}$ 7.1 Hz, CH_3), 4.15 (2H, q, $^3J_{HH}$ 7.1 Hz, CH_2) 6.86 (1H, s, vinyl

proton), 7.02–7.35 (4H, m, arom), 11.46 (1H, br.s, NH). ^{13}C NMR: δ 14.01 (CH_3), 60.28 (OCH_2), 114.01 (=CH) 115.04 (C), 116.98, 123.25, 125.05 and 127.03 (4CH), 132.66 and 140.76 (2C), 154.12 and 165.36 (2C=O).

Propyl-2-(3-oxo-3,4-dihydro-2*H*-1,4-benzothiazin-2-yliden)acetate (6c)

Yellow powder, m.p. 180–182°C, 0.21 g, yield 40%. IR (KBr) ($\nu_{max,}$ cm^{-1}): 3200 (NH), 1716 (C=O), 1600 (C=C). ^{1}H NMR: δ 0.91 (3H, t, $^3J_{HH}$ 7.5 Hz, CH_3), 1.64 (2H, m, CH_2), 4.10 (2H, t, $^3J_{HH}$ 6.5 Hz, CH_2) 6.90 (1H, s, vinyl proton), 7.06–7.63(4H, m, arom), 11.52 (1H, br.s, NH). ^{13}C NMR: δ 10.16 (CH_3), 21.46 (CH_2), 65.77 (OCH_2), 114.08 (=CH), 114.97 (C), 117.00, 123.35, 125.13 and 127.41 (4CH), 132.68 and 140.75 (2C), 154.17 and 165.43 (2C=O).

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