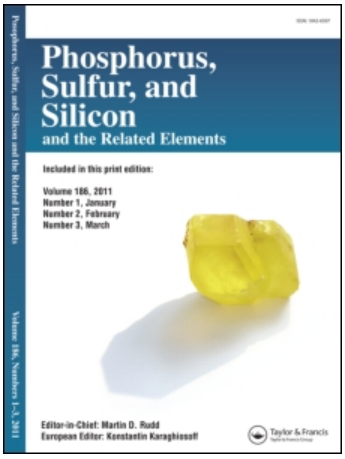

Phosphorus, Sulfur, and Silicon and the Related Elements

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One-Pot Stereoselective Synthesis of Alkyl *Z*-2-[2-Amino-4-oxo-1,3-selenazol-5(4*H*)-yliden] Acetates

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One-Pot Stereoselective Synthesis of Alkyl *Z*-2-[2-Amino-4-oxo-1,3-selenazol-5(4*H*)-yliden] Acetates

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Selenourea reacts with dialkyl acetylenedicarboxylates in acetone to form 1:1 adducts, which undergo a cyclization reaction to produce alkyl Z*-2-(2-amino-4-oxo-1,3-selenazol-5(4*H*)-yliden) acetates in fairly good yields. The reaction is completely stereoselective.*

Keywords 1,3-Selenazol; acetylenic ester; Michael addition; selenourea; stereoselectivity

INTRODUCTION

Although sulfur-containing heterocyclic compound syntheses have been extensively studied, syntheses of selenium analogues have not been appreciably investigated.[1–4] Recently, however, reports of selenium-containing heterocyclic compound synthesis have gradually increased not only because of their interesting reactivities but also because of their

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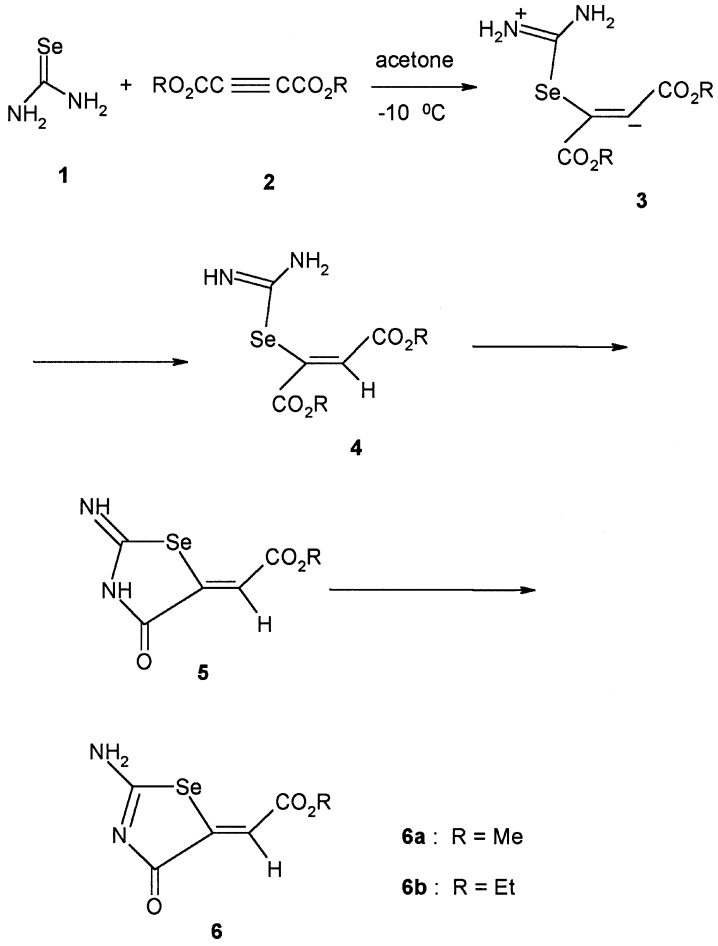
pharmaceutical applications. For example, 1,3-selenazines showed significant antibacterial activity against both Gram-negative and Gram-positive bacteria and potential antitumor effects against several kinds of human cancer cell lines. Selenazofurin demonstrated significant antitumor properties in animals and broad spectrum antiviral activity in cell culture experiments.[3–5] Selenoureas and selenoamides have been used as the precursors for most of the syntheses of 1,3-selenazines and 1,3-selenazoles.[3] Dialkyl acetylenedicarboxylates (**2**) are reactive systems, which take part in many chemical reactions.[6] These results promoted us to examine the one-pot reaction of dialkyl acetylenedicarboxylates (**2**) with selenourea (**1**) (Scheme 1).



SCHEME 1

RESULTS AND DISCUSSION

The compound (**6**) may result from an initial Michael addition reaction of selenourea **1** to the acetylenic ester **2** and concomitant intramolecular protontransfer of the 1:1 adduct **3**, followed by attack of the imine nitrogen on the carbonyl group of the ester to form intermediate **5** (Scheme 1). Intramolecular proton transfer of the intermediate **5** leads to the formation of the alkyl *Z*-2-(2-amino-4-oxo-1,3-selenazol-5(4*H*)-yliden)acetates (**6**) in fairly good yields. TLC indicated that the reaction was completed after 15 min. The reaction proceeds smoothly and cleanly under the reaction conditions. The structures of **6a–b** were deduced from their IR, ^{1}H NMR, and ^{13}C NMR spectra and also via X-ray single crystal (for **6b**) structure determination. The reaction is completely stereoselective.

In summary, we have developed a new and efficient one-pot stereoselective method for preparing compounds **6a–b**. Other aspects of this process are under investigation.

EXPERIMENTAL

Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were measured with a BRUKER DRX-500 AVANCE spectrometer at 500 and 125 MHz, respectively.

General Procedure for the Preparation of Alkyl *Z*-2-(2-Amino-4-oxo-1,3-selenazol-5(4*H*)-yliden) Acetates (6a–b)

A magnetically stirred solution of selenourea **1** (0.123 g, 1 mmol) in acetone (5 mL) was added dropwise a mixture of **2** (1 mmol) in acetone (2 mL) at -10°C over 15 min. The mixture was then stirred at -10°C for 15 min. White crystals of **6** were collected by filtration.

Selected Data for Methyl *Z*-2-(2-Amino-4-oxo-1,3-selenazol-5(4*H*)-yliden) Acetate (6a)

White crystals, m.p. 232.8–233.2°C, yield 58.2%. IR (KBr) (ν_{max}, cm^{-1}): 3217; 3054; 2970; 2823; 1689; 1666; 1496; 1365; 1288; 1180. ^{1}H NMR (DMSO-d_6) δ_H: 3.77 (3H, s, CH_3); 6.95 (1H, s, =CH); 9.4 (1H, s, NH); 9.7 (1H, br. s, NH). ^{13}C NMR (DMSO-d_6) δ_c: 52.65 (CH_3), 118.11 (=CH); 152.44 (=CSe); 167.07 (C-NH_2); 174.69 and 181.00 (2 C=O).

Selected Data for Ethyl *Z*-2-(2-Amino-4-oxo-1,3-selenazol-5(4*H*)-yliden) Acetate (6b)

White crystals, m.p. 214.4–216.9°C, yield 56.5%. IR (KBr) (ν_{max}, cm^{-1}): 3209; 3055; 2985; 2823; 2970; 1705; 1674; 1501; 1280; 1195. ^1H NMR (DMSO-d_6) δ_H: 1.25 (3H, t, $^3J_{HH} = 7.1$ Hz, CH_3); 4.23 (2H, q, $^3J_{HH} = 7.1$ Hz, OCH_2); 6.92 (1H, s, =CH); 9.27 (1H, br. s, NH); 9.76 (1H, br. s, NH).^{13}C NMR (DMSO-d_6) δ_c: 13.99 (CH_3), 61.49 (OCH_2), 118.41 (=CH); 152.21 (=CSe); 166.49 (C-NH_2); 174.71 and 181.01 (2 C=O).

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