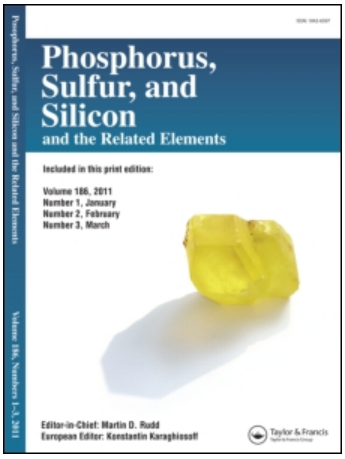

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Triphenylphosphine-Catalyzed Stereoselective Synthesis of Alkyl 3-(2-Naphthylsulfanyl)-2-propenoate from Alkyl Acetylenecarboxylates and 2-Naphthalenethiol

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Protonation of the highly reactive 1:1 intermediates, produced in the reaction between triphenylphosphine and alkyl acetylenecarboxylates by 2-naphthalenethiol, leads to vinyltriphenylphosphonium salts, which undergo an addition–elimination reaction to produce the corresponding S*-vinyl thioethers. The NMR spectra indicated that the compounds contained two stereoisomers for each* S*-vinyl thioether; their ratio was determined on the basis of* ^{1}*H NMR spectra. The reaction is fairly stereoselective.*

Keywords Acetylenic ester; 2-naphthalenethiol; stereoisomers; triphenylphosphine; *S*-vinyl thioether

INTRODUCTION

The phosphorus ylides represent an outstanding achievement of the chemistry of the twentieth century.[1–16] They have found use in a wide variety of reactions of interest to synthetic chemists.[1–16] Phosphorus ylides are important reagents in synthetic organic chemistry,[1–16] especially in the synthesis of naturally occurring products, and compounds with biological and pharmacological activity.[6] The development of the modern chemistry of natural and physiologically active compounds would have been impossible without the phosphorus ylides.[1–16] These compounds have attained great significance as widely used

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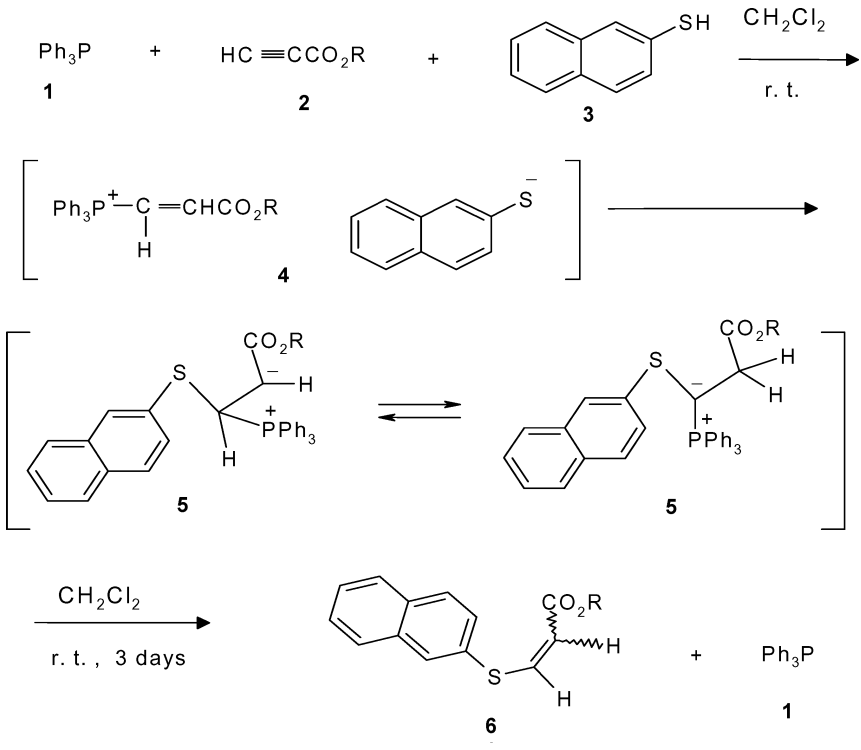
reagents for linking synthetic building blocks with the formation of carbon–carbon double bonds, and this has aroused much interest in the study of the synthesis, structure, and properties of P-ylides and their derivatives.[1–16]

Several methods have been developed for preparation of phosphorus ylides.[1–16] These ylides are most often prepared by the treatment of a phosphonium salt with a base. Most of the phosphonium salts are usually made from phosphine and an alkyl halide,[1–16] and they are also obtained by the Michael addition of phosphorus nucleophiles to activated olefins.[1–16] β-Additions of nucleophiles to the vinyl group of vinylic phosphonium salts leading to the formation of new alkylidenephosphoranes has attracted much attention as a very convenient and synthetically useful method in organic synthesis.[17–30]

Phosphorus ylides are a class of a special type of zwitterions, which bear strongly nucleophilic electron-rich carbanions. The electron distribution around the P^+–C^- bond and its consequent chemical implications has been probed and assessed through theoretical, spectroscopic, and crystallographic investigations.[30] Proton affinity of these ylides can be used as a molecular guide to assess their utility as synthetic reagents and their function as ligands in coordination and organometallic chemistry.[17,30] In the past we established a convenient, one-pot method for preparing stabilized phosphorus ylides utilizing in situ generation of the phosphonium salts.[18–28] Stabilized phosphorus ylides, versatile intermediates in synthetic organic chemistry, can be prepared by the novel reaction of dialkyl acetylenedicarboxylates (DAAD), triphenylphosphine (TPP), and acids such as phenols, imides, amides, enols, oximes, and alcohols (Ali Ramazani reaction).[18–28] The Ali Ramazani reaction[31] involves an intermediate formed by the 1:1 conjugate addition reaction of the TPP to DAAD and concomitant protonation of the intermediate by an acid leading to vinyltriphenylphosphonium salts.[18–28] The salts are unstable intermediates and converted to stabilized phosphorus ylides via Michael addition reaction.[18–28] The stabilized phosphorus ylides are able to take part in the normal intramolecular Wittig reactions, but they are not generally able to participate in the normal intermolecular Wittig reactions.[18–28] The intermolecular Wittig reactions of the ylides are observed only with highly electron-poor carbonyl groups such as indane-1,2,3-trione.[31] The ylides are converted to electron-poor alkenes via elimination of TPP in solvent-free conditions.[31] Almost all of the final products are valuable families of compounds.[31] In this article, we wish to describe a simple method for the stereoselective preparation of alkyl 3-(2-naphthylsulfanyl)-2-propenoates from alkyl acetylenecarboxylates and 2-naphthalenethiol



SCHEME 1

in the presence of triphenylphosphine catalyst in fairly high yields (Scheme 1).

RESULTS AND DISCUSSION

Triphenylphosphine **1**, alkyl acetylenecarboxylates **2**, and 2-naphthalenethiol **3** were reacted in a 1:1:1 ratio in dichloromethane at room temperature to give alkyl 3-(2-naphthylsulfanyl)-2-propenoates **6** (Scheme 1). TLC indicated formation of *S*-vinyl thioethers **6** in CH_2Cl_2. The reaction proceeded smoothly and cleanly under mild conditions, and no side reactions were observed. In the reaction, triphenylphosphine **1** acts as catalyst (Scheme 1). Reactions are known in which an α, β-unsaturated carbonyl compound is produced

from a phosphorane and a carbonyl compound such as an aldehyde or ketone.[19–21] Thus, compounds **6** may be regarded as the product of an addition–elimination reaction. Such addition–elimination products may result from an initial addition of triphenylphosphine **1** to the acetylenic ester **2** and concomitant protonation of the 1:1 adduct, followed by attack of the anion of 2-naphthalenethiol **3** on the vinylphosphonium cation to form intermediate **5**. Elimination of triphenylphosphine**1** from intermediate **5** would lead to stereoselective formation of alkyl 3-(2-naphthylsulfanyl)-2-propenoates (**6**) in fairly high yields (Scheme 1). The mechanism of the reaction outlined above has not been established experimentally. However, a possible explanation[19] is proposed in Scheme 1.

The structure of products **6** was proved by their ^{1}H NMR and ^{13}C NMR spectral data (see the Experimental section). The NMR spectra indicated that solutions of compound **6a–b** ($CDCl_3$ as solvent) contain **Z** isomer as a major product,[19] which may result from the easy formation of ***Z*** isomer to ***E*** isomer. The ratio of the stereoisomers was determined from their ^{1}H NMR spectra. The ^{1}H NMR spectrum of the major (***Z***) stereoisomer of **6a** exhibited four signals readily recognized as arising from one OMe groups ($\delta = 3.82$, s), =CH ($\delta = 5.98$, d, $^{3}J_{HH} = 10.0$ Hz), –SCH= ($\delta = 7.39$,d, $^{3}J_{HH} = 10.0$ Hz) and aromatic moieties ($\delta = 7.43$–8.00, m). The ^{13}C NMR spectrum of the major (*Z*) stereoisomer showed 14 distinct resonances according to expectation. Partial assignment of these resonances is given in the Experimental section. The ^{1}H and ^{13}C NMR signals of the minor stereoisomer (***E***) of **6a** are similar to those of the major stereoisomer (***Z***) of **6a** (see the Spectral Analysis section).[28,32]

CONCLUSION

In summary, we have found a new and efficient method for the stereoselective synthesis of alkyl 3-(2-naphthylsulfanyl)-2-propenoates (**6**) from alkyl acetylenecarboxylates (**2**) and 2-naphthalenethiol (**3**) in the presence of triphenylphosphine (**1**) catalyst (Scheme 1). We believe the reported method offers a simple and efficient route for the preparation of the *S*-vinyl thioethers **6** (Scheme 1). Its ease of workup and the acceptable yields make it a useful method. Possible extensions 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-250 Avance spectrometer at 250.00 and 62.50 MHz.

General Procedure for the Preparation of *S*-vinyl Thioethers 6a–b

To a magnetically stirred solution of triphenylphosphine **1** (0.262 g, 1.00 mmol) and 2-naphthalenethiol **3** (0.16 g, 1.0 mmol) in CH_2Cl_2 (5 ml), a mixture of alkyl acetylenecarboxylate **2** (0.10 mL, 1.0 mmol) in CH_2Cl_2 (2 mL) at $-10^{\circ}C$ was added dropwise over 15 min. The mixture was allowed to warm up to room temperature and stirred for 3 days. The solvent was removed under reduced pressure, and the viscous residue was purified by flash column chromatography (silica gel:petroleum ether-ethyl acetate (10:1)). The solvent was removed under reduced pressure to give products **6a,b**.

Methyl 3-(2-naphthylsulfanyl)-2-propenoate (6a)

Yellow crystal; mp 66.5–67.5 °C; Yield: 80.0%. ^{1}H NMR ($CDCl_3$) (major stereoisomer (***Z***)) δ: 3.82 (3 H, s, OCH_3); 5.98 (1 H, d, $^3J_{HH}$ = 10.0 Hz, =CH); 7.39 (1 H, d, $^3J_{HH}$ = 10.0 Hz, −SCH=) and 7.43–8.00 (7 H, m, aromatic). ^{13}C NMR ($CDCl_3$) (major stereoisomer (***Z***)) δ_c: 51.49 (OCH_3); 113.63 (=CH); 126.00-133.51 (fairly complex, 3 C and 7 CH, aromatic); 149.96 (−SCH=); 166.95 (C=O, ester). ^{1}H NMR ($CDCl_3$) (minor stereoisomer (***E***)) δ: 3.70 (3 H, s, OCH_3); 5.69 (1 H, d, $^3J_{HH}$ = 15.0 Hz, =CH) and 7.43–8.00 (7 H aromatic and 1 H alkene). ^{13}C NMR ($CDCl_3$) (minor stereoisomer (***E***)) δ_c: 51.31 (OCH_3); 115.89 (=CH); 126.00-133.51 (fairly complex, 3 C and 7 CH, aromatic); 147.06 (−SCH=); 165.67 (C=O, ester).

Ethyl 3-(2-naphthylsulfanyl)-2-propenoate (6b)

Yellow solidified oil; Yield: 89.0%. ^{1}H NMR ($CDCl_3$) (major stereoisomer (***Z***)) δ: 1.35 (3 H, t,$^3J_{HH}$ = 7.1 Hz, CH_3); 4.29 (2 H, q,$^3J_{HH}$ = 7.1 Hz, CH_2, Et); 5.96 (1 H, d, $^3J_{HH}$ = 10.0 Hz, =CH); 7.36 (1 H, d, $^3J_{HH}$ = 10.0 Hz, (−SCH=) and 7.43–8.00 (7 H, m, aromatic). ^{13}C NMR ($CDCl_3$) (major stereoisomer (***Z***)) δ_c: 14.40 (CH_3); 60.37 (CH_2, Et); 113.66 (=CH); 126.00–133.72 (fairly complex, 3 C and 7 CH, aromatic); 149.50 (−SCH=); 166.53 (C=O, ester). ^{1}H NMR ($CDCl_3$) (minor stereoisomer (***E***)) δ: 1.25 (3 H, t,$^3J_{HH}$ = 7.1 Hz, CH_3); 4.17 (2 H, q, $^3J_{HH}$ = 7.1 Hz, CH_2, Et); 5.70 (1 H, d, $^3J_{HH}$ = 15.0 Hz, =CH) and 7.43–8.96 (7 H aromatic and 1 H alkene). ^{13}C NMR ($CDCl_3$) (minor stereoisomer (***E***)) δ: 14.30 (CH_3); 60.31 (CH_2, Et); 115.92 (=CH); 126.50–133.80 (fairly complex, 3 C and 7 CH, aromatic); 146.62 (−SCH=); 165.23 (C=O, ester).

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