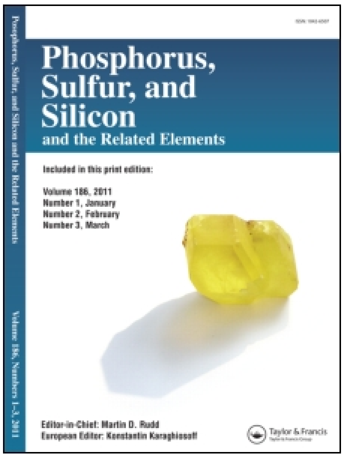

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THE E⇌Z ISOMERIZATION OF 1-METHYLSULFANYLPROPENOIC N-ARYLTHIOAMIDES

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THE E⇄Z ISOMERIZATION OF 1-METHYLSULFANYLPROPENOIC N-ARYLTHIOAMIDES

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1-Methylsulfanylpropenoic N-arylthioamides **2** were shown to undergo the two way **E/Z** isomerization triggered by heat, light and the oxygen and sulfur nucleophiles.

Keywords: 1-methylsulfanylpropenic N-arylthioamides; isomerization; double bond; E and Z isomers

INTRODUCTION

In the ground state, there are substantial energy barriers (around 70 kcal/mol) required for the twisted motions of a double bond to bring about **E/Z** isomerizations.[1] However, under certain conditions, double bonds of alkenes or polyenes prove unstable with respect to both their geometry and position.[2]

For instance, under heat, ultraviolet radiation, strong acids or bases, the **E** and **Z** isomers may equlibrate as shown below[2–4] (Equation 1).

The easy of equilibration, which is reflected in activation energy, appears to increase with a bulk of substituents around the double bond and the **E** isomers generally predominate in such an equlibria. The isomeriza-

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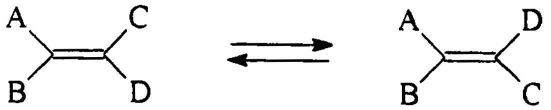
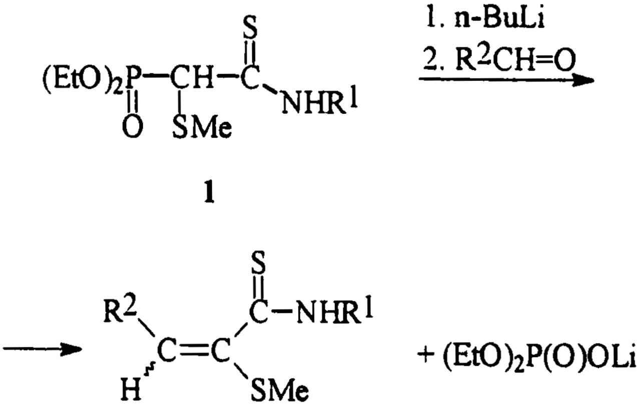


(1)

tion mechanisms for substituted or conjugated double bonds are reported to be unimolecular[3] or bimolecular[4,5] in nature and may involve different intermediates. Most studies of the **E/Z** isomerizations of aliphatic olefins involve activated double bonds such as those of carotenoids, while the most studied **E/Z** isomerizations of aromatic olefins fall within the stilbene family of compounds.[3,6]

Recently, we have elaborated the synthesis of 1-methylsulfanylpropenoic N-arylthioamides **2** utilizing the Horner-Wittig reaction of the lithium salt of **1** with aromatic aldehydes[7] (Equation 2).



1

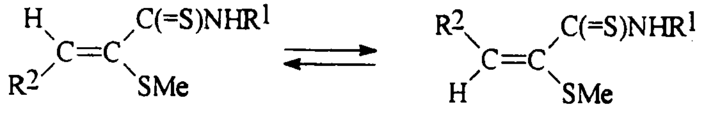
(2)

(E+Z)-2

Moreover, we found that both **E** and **Z** isomers obtained could be easily separated using liquid chromatography over silicagel.[8] Their configuration was firmly confirmed by the n.O.e. measurements. In this paper we would like to publish the results of our further studies on the **E⇌Z** isomerization of **2** upon their exposure to sunlight/dry silicagel, heat or treatment with the oxygen and sulfur nucleophiles.

RESULTS AND DISCUSSION

In the first instance, the photochemical isomerization of the geometrical isomers of **2** was investigated. It was found that the orange or orange-red **Z**-isomers of **2** were converted into the yellow **E**-isomers of **2** in 85–95% yield upon exposure of the former, adsorbed on the TLC plate, to a sunlight for several hours (Equation 3, see Experimental). The results obtained are summarized in Table I.



2-Z **2-E** (3)

TABLE I Photochemical and thermal isomerizations of **2**

No	*Compound*	*Yield [%]*	
		Photochemical isomerization Z→E, E (%)	*Thermal isomerization E→Z, Z (%)*
2a	$PhCH{=}C(SMe)C({=}S)NHC_6H_4p\text{-}Cl$	84	63
2b	$PhCH{=}C(SMe)C({=}S)NHC_6H_4p\text{-}Br$	93	69
2c	$p\text{-}Br\text{-}C_6H_4CH{=}C(SMe)C({=}S)NHC_6H_4\text{-}p\text{-}Cl$	80	55
2d	$p\text{-}Br\text{-}C_6H_4CH{=}C(SMe)C({=}S)NHEt$	88	56

In a separate experiment, it was shown that the **Z** isomers of **2** did not isomerize in solution even in a contact with silicagel. Thereby, it was also proved that the **Z**$\rightleftharpoons$**E** isomerization of **2** did not occur by the solvent (benzene) photosensitization what was successfully applied for some reactions requiring small activation energies (see, for example isomerization of butene-2 and pentene-2[9]). Moreover, it was confirmed, that the small pH deviations (±0.5) from the neutral pH, admissible for the Merck silicagel 60, had no influence on isomerization in solution. Having this in mind, one can conclude that the isomerization of **Z-2** is connected with the lowering of the activation energy on dry silicagel required to break an olefinic bond and to form the radical type species. The lowering of the energy is attributed not only to a magnitude of adsorption forces on a solid support,[10] but also is connected with a nature of the conjugated thioamide moiety which relatively easy undergoes photosensitization and should reveal different UV absorption for both **E** and **Z** isomers. Indeed, the UV absorption spectra of the **E** and **Z** isomers are distinctly different. For instance, the **Z-2b** isomer absorbs sunlight energy more intensively showing two high maxima at 318 and 228 nm while **E-2b** isomer shows only one maximum at 238 nm what enables the shift of the position of the photochemical **E/Z** equilibrium towards formation of the **E** isomer. For a comparison, the reactive excited state for the thioketone moiety in aromatic thioketones is (n, π^*) and photochemical reactions can be effected with radiation of the wave length either 316/366 or 586 nm.[11]

The thermal isomerization caused the 55–69% conversion of the yellow E-isomers into the orange or the orange-red **Z** isomers (see Table I). In a typical experiment, **E-2b** was heated without solvent in a sodium glass vial at 90–95°C and a mixture of **E-2b** and **Z-2b** was obtained in a 1:1 ratio after 3–4 hours. After 44 hours this ratio was 3:7. In order to exclude a catalytic effect of the sodium glass on isomerization, **E-2b** was heated in a chemically inert, Teflon® tube under moisture free, argon atmosphere for a few hours and the products were obtained in the same **E/Z**=1:1 ratio, as in the glass.

Our investigations aimed at functionalization of **2** by the conjugate addition of the O,S-nucleophiles, like phenolates and thiolates revealed that the expected 1,4-adducts were not formed under the reaction conditions. For instance, starting from **Z-2a** and sodium benzenethiolate or sodium p-chlorophenolate as nucleophiles, a mixture of the geometrical isomers of **2** was obtained at room temperature in both cases, instead of the expected 1,4-adducts (Table II). In this mixture, the opposite **E** isomer predominated. It was found that the equimolar amount of the nucleophile should be used, otherwise the yield of the **E** isomer remained low. Sodium benzenethiolate as a better nucleophile gave higher reaction yields within shorter reaction times than sodium p-chlorophenolate. Further optimization of the reaction conditions led to the observation that silylation of the NH group by trimethylsilyl chloride[12,13] in **Z-2a** gave the highest yield of isomerization with benzenethiolate. Both this observation and interpretation of other results presented in Table II may be rationalized by the competitive interaction of the O,S- nucleophiles with the acidic NH hydrogen atom.

TABLE II Isomerization of **Z-2a** with O,S-nucleophiles

Reaction conditions	*Z/E ratio*	*E (%)*
PhSNa (cat.), 25°C, 2 days	11:3	21
PhSNa (1 eq.), 25°C, 2 days	1:4	80
PhSH (1 eq.), Al_2O_3 (I act.), 1 day	17:2	10
n-BuLi (0°C), TMS-Cl (0°C); PhSLi (0°, 25°C)	1:12	92
p-Cl-C_6H_4ONa, 2 weeks, 25°C	8:9	52

The most likely mechanism of the above described isomerization involves a reversible attack of the O,S-nucleophile at the double bond to cause its break, rotation around the developed single bond and reconstruction of the double bond possessing a changed stereoconfiguration.[14]

In summary, we described herein three different ways of the controlled **E/Z** isomerization of 1-methylsulfanylpropenoic N-arylthioamides **2**. The photochemical and nucleophile catalyzed izomerization affords a possibility for the **Z**$\rightleftharpoons$**E** conversion while the thermal one enables the reverse process to occur.

EXPERIMENTAL

Propenoic N-arylthioamides were prepared according to the literature procedure.[7] Inert solvents: benzene or toluene, occasionally with n-hexane as a cosolvent were used for chromatography over silicagel, TLC development or sample transfers. For the photochemical isomerization, samples of propenoic N-arylthioamides **2** were adsorbed on the TLC preparative plates (Merck, Kieselgel $60F_{254}$) and were exposed to a sunlight in a typical, cloudless, sunny day (~100 kLx, 10–20 mW/cm^2). The TLC warming was minimized. ^{1}H-NMR spectra were recorded with a Bruker MSL spectrometer operating at 300 MHz. The reaction progress was monitored using Merck analytical plates ($60F_{254}$).

Photochemical isomerization

Method A

A mixture of the **E** and **Z** isomers of propenoic N-arylthioamides **2a-c** (0.3 mmol) was dissolved in benzene, adsorbed on the preparative TLC plate, developed in benzene into two spots representing separate **E** and **Z** isomers, dried in a stream of argon and exposed to a sunlight for 7–10 hours. After separation of both spots, ^{1}H-NMR spectra revealed mostly the original, unchanged **E** isomer in one spot and a mixture of **E** and **Z** isomers in which the **E** isomer predominated in another spot (80–93% yield, see Table I).

Method B

A mixture of **(E+Z)-2b** was separated by column chromatography, adsorbed separately on the preparative TLC, exposed to a sunlight and analyzed with the ^{1}H-NMR technique as in Method A.

Thermal isomerization

The **E**-isomers of **2a-c** (0.1 mmol) were placed in a glass vial or Teflone® tube and heated to the temperature of 5–10°C below the melting point (**2a**, **2d**~90°C; **2b**~95°C; **2c**~130°C). The glass vial was put into the heater. The Teflone® tube was protected on both side against moisture, rinsed with a stream of argon and immersed in an oil bath. In both cases the 50% **E**→**Z** conversion was achieved within a few hours. A further 10–20% increase of the yield required heating for 44 hrs, such as for **2b** (see Table I).

Isomerization of 2 with O,S-nucleophiles

Method A

To a solution of **Z-2a** (0.25 mmol, 71 mg) in ethanol (10 ml), a solution of sodium benzenethiolate (0.25 mmol; prepared from thiophenol and sodium in ethanol) or sodium p-chlorophenolate (0.25 mmol; prepared from p-chlorophenol and sodium in ethanol) in ethanol (3 ml) was added and the resulting mixture was stirred at room temperature under argon for the time indicated in Table II. The reaction mixture was neutralized with aqueous saturated solution of NH_4Cl, extracted with ether, dried over $MgSO_4$, filtered and evaporated to give a mixture of isomers containing 52–80% of the **E** isomer.

Method B

To a stirred solution of **Z-2a** (0.25 mmol, 71 mg) in dry tetrahydrofuran (6 ml), a solution of n-butyllithium (0.25 mmol) in n-hexane was added at 0°C under argon atmosphere. Then trimethylsilyl chloride (0.25 mmol, 27 mg) was added followed by a tetrahydrofuran solution of lithium benzenethiolate (0.25 mmol, prepared separately from 27.5 mg PhSH and 0.25 mmol n-BuLi in THF at 0°C). After the last addition was completed, the reaction mixture was warmed to room temperature and worked-up as in the Method A [**Z**→**E** (92%)].

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