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Photochemical Reactivity of 2-Azido-1,3-thiazole and 2-Azido-1,3-benzothiazole: A Procedure for the Aziridination of Enol Ethers

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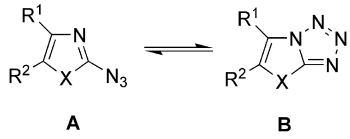
Direct irradiation of a mixture of the azido–tetrazole tautomers of 2-azido-1,3-thiazole and 2-azido-1,3-benzothiazole in toluene solution gives products arising from the intermediate nitrene, which in turn undergoes ring opening in the case of 2-azido-1,3-thiazole to give a polymer, and dimerization in the case of 2-azido-1,3-benzothiazole to give [1,3]benzothiazolo[2′,3′:3,4][1,2,4,5]tetraazino[6,1*b*][1,3]benzothiazole in low yields. When irradiation is performed in the presence of methyl acrylate or various enol ethers, aziridination of the double bond is observed, with good yields in the case of enol ethers. Among these, 1-(6-methyl-3,4-dihydro-2*H*-pyran-2-yl)ethanone undergoes aziridination with complete diastereoselectivity to give the (1*RS*,3*RS*,6*SR*) diastereomer.

Introduction

Most work on the simple molecules 2-azido-1,3-thiazole (**1**), 2-azido-1,3-benzothiazole (**2**) and 2-azido-1-methyl-1*H*-imidazole (**3**; Scheme 1) has focused on azido–tetrazole isomerism, which has been extensively studied from chemical[1] and theoretical viewpoints.[2] Among these compounds, **3** does not isomerize,[3] and it undergoes photochemical ring cleavage[4] that provides a facile route to small molecules such as heterodienes, which are useful building-blocks in hetero-Diels–Alder reactions.[5] These studies indicated that the azido–tetrazole equilibrium is normally affected by the solvent and temperature. In the instances of **1** and **2**, the azido forms were found to be more favoured by decreasing the solvent polarity and by increasing the temperature.[6] In light of these results, we would expected that the photochemical reactivity of azido–tetrazole mixtures **1** and **2** does not differ substantially from the photochemical behaviour of azide **3**, even if this latter was carried out in water.[4]

This study was carried out in view of the chemical,[7] biological[8] and pharmacological[9] importance of these nitrogen-linked azole systems and to find the influence on the photochemical reactivity of the cyclized or open-chain forms.

Azides, via nitrene intermediates, can also be useful synthetic starting materials for the preparation of aziridines.



1: $R^1 = R^2 = H$; X = S
2: $R^1–R^2 = C_4H_4$; X = S
3: $R^1 = R^2 = H$; X = N-CH_3

Scheme 1. Equilibrium between the two forms of the azide.

These in turn act as nitrogen-like analogues of epoxides, undergoing ring opening to give amines. The aziridine moiety is also involved in natural products like mitosanes and azinomicynes,[10] with strong antibiotic and/or antitumour activity. As a further development of our study, we want to report a comparison between the thermal and photochemical aziridination of methyl acrylate with thiazole **1** via nitrene and also to report an unprecedented photochemical procedure for the aziridination of enol ethers in good yields.

Results and Discussion

Photolysis of 2-Azido-1,3-thiazole (1) and 2-Azido-1,3-benzothiazole (2)

Usually, azides **1** and **2** are obtained by diazotization of the corresponding heteroarylamines followed by addition of sodium azide to the former diazonium salts,[11] or alternatively, by nitrosation of 2-hydrazinothiazoles.[12] Very recently, these azides were prepared by an azido transfer reaction. In line with the strong-base-proton-exchange process, preparative butyllithium deprotonation at the 2-position of the azoles and subsequent reaction with tosyl azide affords

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the corresponding lithium triazene salts, from which azides **1** and **2** can be isolated after aqueous tetrasodium pirophosphato fragmentation.[13]

The equilibrium between linear form **A** and tetrazolic form **B** of azides (Scheme 1) derived from suitable nitrogen-containing heterocycles is a well-known process, and in our case, it was confirmed by ^{1}H NMR spectroscopy in $CDCl_3$, with a 5:1 ratio in favour of the linear form (Figure 1). Although this ratio depends on the solvent used (see below), it is reasonable that in toluene a certain amount of the tetrazole form exists, as was confirmed by ^{1}H NMR spectroscopy of **1** in [D_6]benzene, which gave a 5.6:1 ratio in favour of the linear form.

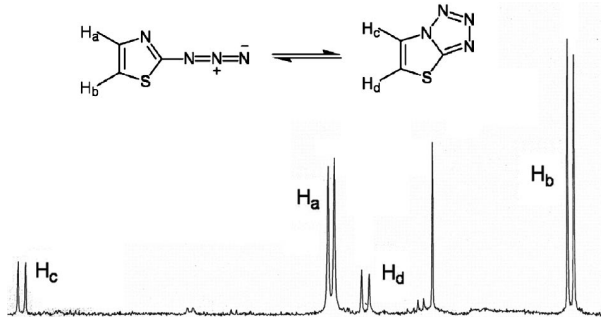


Figure 1. ^{1}H NMR spectrum of **1** in $CDCl_3$.

The irradiation of **1** in toluene for 3 d gave, together with unreacted starting material, a pale-brown powder that was identified, according to gel permeation chromatography (GPC) analysis, as a polymeric product. The distribution of the molecular weights of the polymer is shown in Figure 2. On the basis of spectroscopic data it was not possible to give an exact structure of this polymer. Clearly, it comes from ring opening of **1**, because we observed the presence of nitrile adsorption in the IR spectrum, as well as a signal at δ = 119.23 ppm in the ^{13}C NMR spectrum (see Experimental Section).

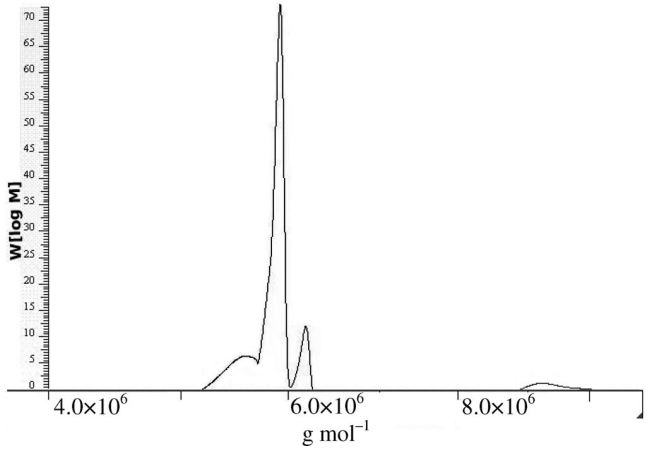
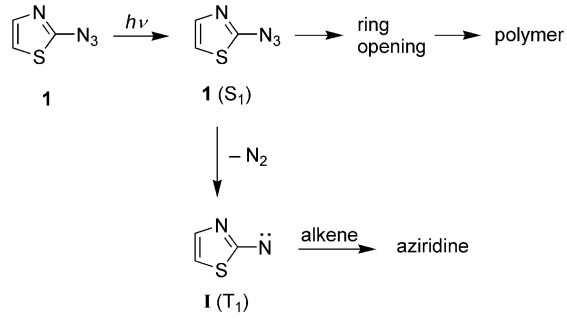


Figure 2. GPC analysis of polymer from **1**.

On the basis of theoretical calculations (see below), it can be supposed that irradiation of **1** gave the corresponding singlet state, which can either undergo ring opening or, after nitrogen loss, give directly triplet nitrene **I**, which in turn can insert into double bonds to give aziridines (Scheme 2).



Scheme 2. Pathway of **1** after irradiation.

Also, in the case of **2**, we observed in solution both the linear and the tetrazolic form, and a 11:1 ratio in favour of the linear form was measured in DMSO, whereas a 1:1 ratio was obtained in $CDCl_3$ (Figure 3); furthermore, a measure in [D_6]benzene gave a 2.5:1 ratio. A toluene solution of **2** when irradiated did not undergo ring opening because of the greater stability of the benzothiazole ring, but gave in low yield dimer **4**, according to the mechanism outlined in Scheme 3, also in this case involving a nitrene intermediate. This compound was identified by ^{1}H NMR spectroscopy and by comparison of its IR data with those reported by Eichenberger et al.,[14] who obtained **4** by a different synthetic way.

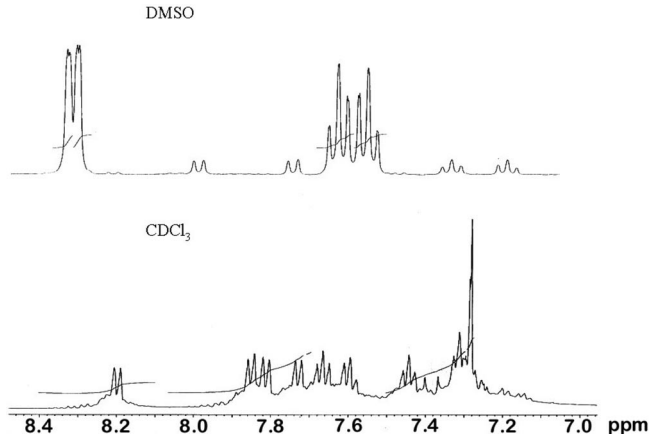
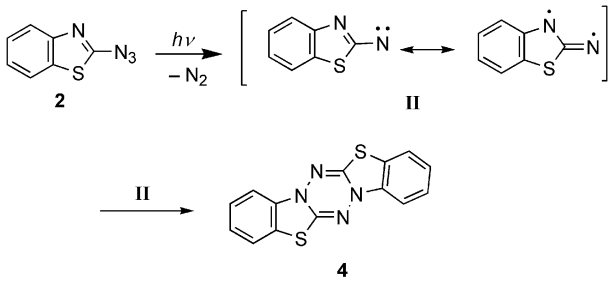


Figure 3. ^{1}H NMR spectra of **2**.

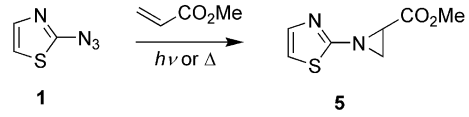
We have also performed the same reaction on **2** at higher temperature (60 °C) with the aim to induce ring opening of suggested intermediate **II**, but the only effect was a slight increase in the yield of **4** (9%). These results suggest that azides derived from condensed systems could have a greater stability than those of simple pentaatomic systems, which readily undergo ring opening and/or ring fragmentation processes.[15]



Scheme 3. Formation of **4**.

Thermal vs. Photochemical Reactivity of 2-Azido-1,3-thiazole (1) with Methyl Acrylate

With the aim to investigate the synthetic utility of the so-generated nitrenes, we performed the photochemical reaction of **1** in the presence of some electron-withdrawing substituted alkenes, for example, methyl acrylate, acrylonitrile, acrylamide and methyl vinyl ketone, comparing the reactivity with their thermal counterparts. Only in the case of methyl acrylate did we observe photochemical or thermal reactivity, whereas in the other cases, no product was detected (Scheme 4).



Scheme 4. Reaction of 2-azido-1,3-thiazole (**1**) with methyl acrylate.

The irradiation of **1** with methyl acrylate in toluene afforded, after 5 d, aziridine **5** in very low yield (3.6%) together with unreacted azide and the above-described polymer. The same product with comparable yield was observed in the thermal reaction of **1** and methyl acrylate in toluene at 25 °C. Aziridine **5** was identified by mass spectrometry (184, $[M]^+$) and by comparing the ^1H and ^{13}C NMR spectroscopic data with those of similar aziridines and triazolines reported in the literature: in fact, δ values for the protons of the triazoline ring are higher than those of the aziridine ring[16] and the same behaviour was observed for ^{13}C chemical shifts.[17] This comparison was important because thermal reactions of azides with alkenes or alkynes could give rise to triazolines or triazoles, respectively,[18] where in the mass spectra a ion at $[M - 28]^+$ due to the loss of nitrogen was observed instead of the molecular ion. We did not detect any triazoline in this kind of reaction.

Insertion of nitrenes, thermally or photochemically generated, into double bonds is a well-known process in synthetic organic chemistry.[10] Depending on reaction conditions and substituents on the nitrogen atom, nitrenes can be generated in the singlet or triplet state. Usually, the former are more reactive, being able to form both new bonds in a concerted process, and thus allowing in some cases to perform reactions in a stereoselective fashion.[19] On the contrary, triplet nitrenes are more stable, and they react with alkenes in a two-step way, involving the formation of a diradical, which is able to undergo bond rotation. So, insertion reactions of triplet nitrenes do not show high stereoselectivity.

To better understand the role of light in aziridine formation, a kinetic study was performed on both thermal and photochemical reactions for a prolonged time. Owing to the low yields of the product, the reactions were followed by GC–MS, monitoring for each reaction the ratio between the abundance of the ion at m/z = 184 ($[M]^+$ of **5**) and that of the ion at m/z = 126 ($[M]^+$ of **1**). Results are outlined in Figure 4. It is clear that photochemical conditions performed with prolonged reaction times allowed higher yields of the reaction product to be obtained.

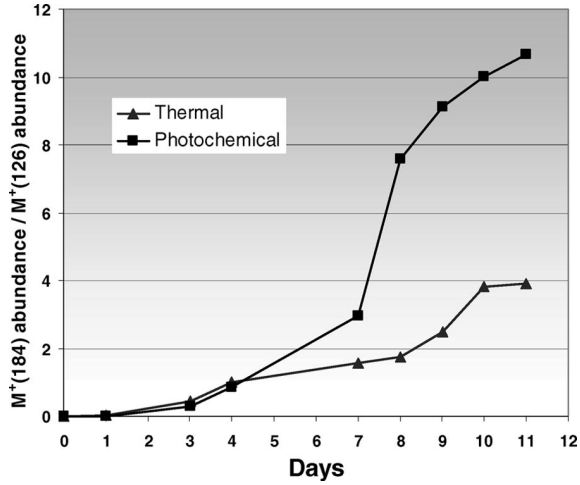
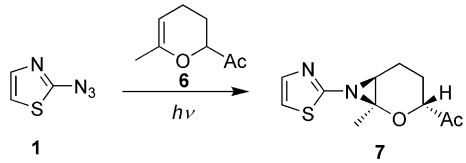


Figure 4. Kinetic of thermal vs. photochemical reaction of **1** with methyl acrylate.

Aziridination of Enol Ethers

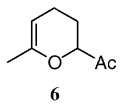
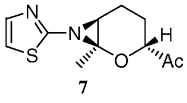
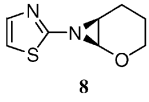
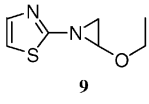
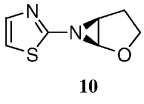
When the photolysis of **1** was performed in the presence of various enol ethers, aziridination of the double bond in good yields was observed. This behaviour was casually discovered by measuring the thermal and photochemical reactivity of **1** with methyl vinyl ketone: in fact, whereas this latter did not react in either way, the diastereoselective formation (see below) of **7** was observed (Scheme 5) as a result of the presence of variable amounts of enol ether **6** (known also as "methyl vinyl ketone dimer") in commercial methyl vinyl ketone, which in turn comes from the hetero-Diels–Alder reaction of methyl vinyl ketone with itself.[20]



Scheme 5. Photochemical aziridination of enol ether **6**.

These findings prompted us to investigate this kind of reactivity with pure **6** and other available enol ethers. Results are summarized in Table 1.

Table 1. Aziridination of enol ethers.

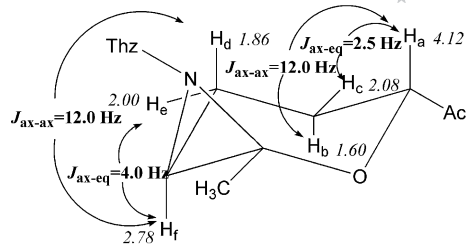
Enol Ether	Aziridine	Yield[a] [%]
 **6**	 **7**	79
	 **8**	46
	 **9**	42
	 **10**	42

[a] All yields refer to chromatographically pure products.

It must be noted that: (i) The reactions can be obtained only by using a photochemical procedure: thermal reactions set up under the same conditions for control did not show formation of any product. (ii) Yields are far higher than those reported with methyl acrylate. (iii) Benzothiazole **2** does not react under the same conditions. (iv) Only a few examples[21] of the photochemical aziridination of an enol ether are reported in the literature, but in these cases, the reaction proceeds by a thermal dipolar cycloaddition of the azide to give a triazoline, which in turn is photochemically converted into an aziridine; we instead observed direct formation of the aziridine. (v) When performed on enol ether **6**, the reaction is diastereoselective, giving rise only to the (1*RS*,3*RS*,6*SR*) diastereomer. The relative stereochemistry was established by measuring the coupling constants (Scheme 6), after assignment of all the proton signals (COSY): all *J* values are in agreement with the proposed stereochemistry.

Although insertion of triplet nitrenes usually shows poor stereoselectivity, in this case, the observed complete diastereoselectivity could be ascribed to thermodynamic control, leading to the isomer having the two bulky groups (methyl and acetyl) in an equatorial position.

In order to understand the observed photochemical behaviour, we performed some theoretical calculations. We performed DFT and TD-DFT calculations at the B3LYP/6-31G+(d,p) level on Gaussian 03.[22] The excitation of **1** (total energy = –732.65416054 H) gave the corresponding excited singlet state (ΔE = 4.57 eV). Attempts to obtain triplet **1** failed. In this case, only nitrene **I** was obtained (total energy = –632.12380551 H). Then, probably, the excited singlet state decays directly into triplet nitrene **I**. We also attempted to characterize the singlet nitrene, but DFT methods cannot be used for this purpose. Hartree–Fock calculations [at the 6-31G-(d,p) level] showed that singlet nitrene **I** did not exist. In agreement with the experimental results reported above, we found that in this case the S–C2 bond is broken. The triplet nitrene showed the LSOMO orbital at –0.280 H as a σ orbital and the HSOMO orbital at –0.256 H as a π orbital (Figure 5).



Scheme 6. Diagnostic coupling constants in **7** (δ values are in italic).

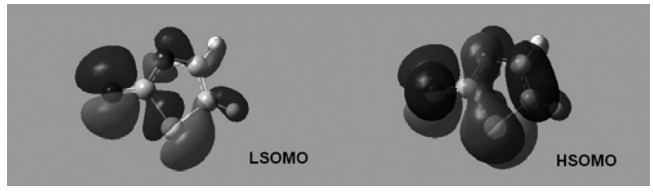


Figure 5. LSOMO and HSOMO of nitrene **I**.

Methyl acrylate in the ground state showed the HOMO orbital at –0.283 H (σ orbital) and the LUMO orbital at –0.070 H (π* orbital). The best interaction between the triplet nitrene frontier orbitals and those of methyl acrylate can be obtained between the LSOMO of the nitrene and the HOMO of methyl acrylate. Both the orbitals are σ orbitals. Acrylonitrile did not react with **1**. To confirm our approach we performed calculations on this compound, too. Acrylonitrile in the ground state showed the HOMO orbital at –0.300 H (π orbital), whereas the LUMO orbital is a π* orbital at –0.072 H. The best interaction is that between the σ LSOMO of triplet nitrene and the π HOMO orbital of acrylonitrile.

3,4-Dihydro-2*H*-pyran in its ground state showed the HOMO at –0.221 H as a π orbital, whereas the LUMO is at 0.004 H (Figure 6). In this case, the best interaction between the frontier orbitals is that between the HSOMO of the nitrene and the HOMO of the dihydropyran. Both the orbitals are π orbitals. The same behaviour was observed when the calculations were performed on 2,3-dihydrofuran. Also in this case, the HOMO is at –0.215 H, and it is a π orbital, whereas the LUMO is at 0.010 H. Also, in this case,

the best interaction between the frontier orbitals is that between the π HSOMO of the nitrene and the π HOMO of the dihydrofuran.

Figure 6. Frontier orbitals of dihydropyran.

Conclusions

In summary, we studied the photochemical reactivity of 2-azido-1,3-thiazole and 2-azido-1,3-benzothiazole, showing that these compounds, if they react alone, can give rise to self-condensation or polymerization and, in the presence of double bonds, to aziridines (for 2-azido-1,3-thiazole) via the nitrene intermediates. In the case of enol ethers, the very simple procedure, the high yields and the diastereoselectivity obtained in one case make this kind of reaction valuable for synthetic purposes.

Experimental Section

General: Column chromatography was carried out on Merck silica gel (0.063–0.200 mm particle size) by progressive elution with the appropriate solvent mixture. ^{1}H and ^{13}C NMR spectra were normally carried out in $CDCl_3$ or [D_6]DMSO solutions with a Bruker AM 300 MHz or a Varian Inova 500 MHz. IR spectra were carried out with a Perkin–Elmer 883. Mass spectra were obtained with a Hewlett–Packard 5971 mass-selective detector with a Hewlett–Packard 5890 gas chromatograph in SIM mode (single-ion monitoring) for compound **5** or with an LC–MS equipped with ionic trap for polymer from **1**. Gas chromatographic analyses were obtained by using an OV-1 capillary column in the range 70–250 °C (20 °C min^{-1}). Gel permeation chromatography (GPC) was performed with an HP 1100 HPLC system equipped with a diode-array detector, a PLGel column (eluant: *n*-hexane). Toluene was degassed for 1 h under vacuum. 2-Amino-1,3-thiazole and 2-amino-1,3-benzothiazole were purchased from Aldrich. 2-Azido-1,3-thiazole (**1**) and 2-azido-1,3-benzothiazole (**2**) were prepared according to the literature. Enol ether **6** was obtained by fractional distillation of an aged (6 months) sample of methyl vinyl ketone: b.p. 65–70 °C (20 Torr; 1 Torr = 133.3 Pa), ref.[20] 68 °C (13 Torr). All irradiations were done in an immersion apparatus with a 125 W high-pressure mercury arc lamp (Helios-Italquartz) surrounded with a water-cooled Pyrex jacket for the appropriate time.

Photolysis of 1: Thiazole **1** (630 mg, 5 mmol) was dissolved in toluene (100 mL) and irradiated for 3 d with stirring. At this time, TLC revealed that azide was still present and a powder precipitate was observed on the bottom of the vessel. The solution was then filtered, and the solid was washed with toluene, collected and dried under vacuum to obtain a polymeric powdered product (130 mg). IR (KBr): $\tilde{\nu}$ = 2240, 2200 cm^{-1}. UV/Vis (CH_3CN): λ = 207, 250 nm, ^{1}H NMR (500 MHz, [D_6]DMSO, most abundant signals): δ = 8.30 (br. s), 8.27 (s), 7.52 (d, J = 7.6 Hz), 7.27 (m), 7.04 (s), 6.92 (s), 6.76 (d, J = 11.6 Hz), 6.32 (s), 6.15 (br. s), 3.58 (br. s), 2.21 (s) ppm. ^{13}C NMR (125 MHz, [D_6]DMSO): δ = 163.74, 124.06, 119.23 ppm. MS: *m*/*z* = 145, 73. GPC: Mn: 5.925×10^6, Mw: 5.9823×10^6, Mz: 6.0668×10^6, Mv: 5.9823×10^6. Found: C 32.09, H 5.42, N 33.43, S 28.72.

Photolysis of 2: Benzothiazole **2** (880 mg, 5 mmol) was dissolved in toluene (100 mL) and irradiated for 3 d with stirring. At this time, TLC revealed that azide was still present and the formation of a product at a low R_f value (no precipitate was observed). The solution was then evaporated, and the crude mixture was chromatographed on silica gel ($CHCl_3$/MeOH, 97:3) to obtain **4** (46 mg, 5%) as a brown powder. M.p. 204–206 °C (ref.[14] 207–208.5 °C). ^{1}H NMR (300 MHz, [D_6]DMSO): δ = 7.90–7.52 (m, 4 H), 7.48–7.20 (m, 4 H) ppm. ^{13}C NMR (75 MHz, [D_6]DMSO): δ = 130.76, 125.76, 123.03, 122.34, 122.06, 121.49, 116.03 ppm. IR: $\tilde{\nu}$ = 3853, 3839, 1618, 1514, 1339, 1261, 1213, 979 cm^{-1}. $C_{14}H_8N_4S_2$ (296.37): calcd. C 56.74, H 2.72, N 18.90, S 21.64; found C 56.55, H 2.70, N 19.01, S 21.59.

Photolysis of 2 at 60 °C: Benzothiazole **2** (176 mg 1 mmol) was dissolved in toluene (20 mL) and irradiated in a thermostatted Pyrex vessel at 60 °C. After 3 d, the solution was evaporated, and the crude mixture was chromatographed on silica gel ($CHCl_3$/MeOH, 97:3) to obtain **4** (16 mg, 9%).

Photolysis of 1 with Methyl Acrylate: To a solution of thiazole **1** (630 mg, 5 mmol) dissolved in toluene (100 mL) was added with methyl acrylate (4.3 g, 50 mmol), and the mixture was irradiated for 5 d without stirring. Stirring is to be avoided to allow the polymer to settle on the bottom of the vessel, and so to maintain the solution clear. The solution was then filtered to discard the polymer, and the solvent was evaporated under vacuum to afford a crude mixture (270 mg) that was chromatographed over silica gel to afford **5** (34 mg, 3.6%) as an oil. MS: *m*/*z* (%) = 184 [M]$^+$, 169, 125. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.31 (d, J = 4.0 Hz, 1 H), 6.94 (d, J = 4.0 Hz, 1 H), 3.80 (s, 3 H), 3.23 (dd, J = 6.5, 3.5 Hz, 1 H), 2.73 (dd, J = 3.5, 1.5 Hz, 1 H), 2.70 (dd, J = 6.5, 1.5 Hz, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 173.15, 167.95, 138.07, 114.72, 51.67, 38.64, 34.87 ppm. $C_7H_8N_2O_2S$ (184.22): calcd. C 45.64, H 4.38, N 15.21, S 17.41; found C 45.53, H 4.34, N 15.24, S 17.35.

General Procedure for the Aziridination of Enol Ethers: To a solution of thiazole **1** (630 mg, 5 mmol) dissolved in acetonitrile (100 mL) was added an excess amount of the appropriate enol ether (50 mmol), and the mixture was irradiated for 5 d without stirring (vide supra). The solution was then filtered to discard the polymer, and the solvent was evaporated under vacuum to afford a crude mixture that was chromatographed over silica gel (*n*-hexane/ethyl acetate, 9:1) to obtain the pure aziridines.

7: Oil (940 mg, 3.95 mmol, 79%). MS: *m*/*z* = 238 [M]$^+$, 140, 97. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.24 (d, J = 8.0 Hz, 1H), 5.22 (d, J = 8.0 Hz, 1 H), 4.12 (dd, J = 12.0, 2.5 Hz, 1 H), 2.78 (dd, J = 12.0, 4.0 Hz, 1 H), 2.27 (s, 3 H), 2.08 (m, 1 H), 2.00 (m, 1 H), 1.86 (dq, J = 13.5, 4.0 Hz, 1 H), 1.75 (s, 3 H), 1.60 (dq, J = 13.0, 3.5 Hz, 1 H) ppm. ^{13}C NMR and DEPT (125 MHz, $CDCl_3$): δ = 206.56 (C), 122.01 (CH), 112.17 (C), 97.38 (CH), 86.27 (C), 76.61 (CH), 41.12 (CH), 27.31 (CH_2), 27.05 (CH_3), 26.98 (CH_2), 26.36 (CH_3) ppm. $C_{11}H_{14}N_2O_2S$ (238.30): calcd. C 55.44, H 5.92, N 11.76, S 13.46; found C 55.32, H 5.86, N 11.70, S 13.39.

8: Oil (423 mg, 2.32 mmol, 46%). MS: *m*/*z* = 182 [M]$^+$, 149, 97, 84. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.12 (d, J = 8.0 Hz, 1H), 5.19 (d, J = 8.0 Hz, 1 H), 5.01 (br. s, 1 H), 3.88 (m, 1 H), 3.64 (m, 1 H), 3.16 (br. s, 1 H), 1.93–1.79 (m, 4 H) ppm. ^{13}C NMR and DEPT (125 MHz, $CDCl_3$): δ = 121.17 (CH), 113.35 (C), 99.30 (CH), 82.72

(CH), 65.31 (CH_2), 36.69 (CH), 26.52 (CH_2), 22.83 (CH_2) ppm. $C_8H_{10}N_2OS$ (182.24): calcd. C 52.72, H 5.53, N 15.37, S 17.59; found C 52.78, H 5.57, N 15.31, S 17.66.

9: Oil (355 mg, 2.09 mmol, 42%). MS: *m*/*z* = 170 $[M]^+$, 141, 125, 113. ^1H NMR (500 MHz, $CDCl_3$): δ = 6.20 (d, *J*=8.0 Hz, 1H), 5.40 (d, *J* = 8.0 Hz, 1 H), 5.09 (br. s, 1 H), 3.92 (p, *J* = 7.0 Hz, 1 H), 3.73 (p, *J* = 7.0 Hz, 1 H), 2.97 (d, *J* = 13.0 Hz, 1 H), 2.91 (d, *J* = 13.0 Hz, 1 H), 1.27 (t, *J* = 7.0 Hz, 3 H) ppm. ^{13}C NMR and DEPT (125 MHz, $CDCl_3$): δ = 119.83 (CH), 114.31 (C), 102.33 (CH), 82.85 (CH), 65.08 (CH_2), 29.54 (CH_2), 15.07 (CH_3) ppm. $C_7H_{10}N_2OS$ (170.23): calcd. C 49.39, H 5.92, N 16.46, S 18.84; found C 49.44, H 5.89, N 16.47, S 18.89.

10: Oil (214 mg, 1.27 mmol, 42%). MS: *m*/*z* = 168 $[M]^+$, 139, 107, 70. ^1H NMR (500 MHz, $CDCl_3$): δ = 6.34 (d, *J*=8.0 Hz, 1H), 5.27 (d, *J* = 8.0 Hz, 1 H), 5.21 (d, *J* = 4.5 Hz, 1 H), 4.29 (dt, *J* = 9.0, 4.0 Hz, 1 H), 4.10 (q, *J* = 4.5 Hz, 1 H), 3.50 (m, 1 H) 2.38 (m, 1 H), 2.10 (m, 1 H) ppm. ^{13}C NMR and DEPT (125 MHz, $CDCl_3$): δ = 123.06 (CH), 112.90 (C), 97.45 (CH), 84.78 (CH), 68.10 (CH_2), 39.18 (CH), 29.63 (CH_2) ppm. $C_7H_8N_2OS$ (168.22): calcd. C 49.98, H 4.79, N 16.65, S 19.06; found C 50.03, H 4.81, N 16.61, S 19.11.

Supporting Information (see footnote on the first page of this article): Selected MS, GC–MS, UV/Vis, IR ^1H NMR, ^{13}C NMR, DEPT and COSY spectra; Cartesian coordinates and Z matrix.

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