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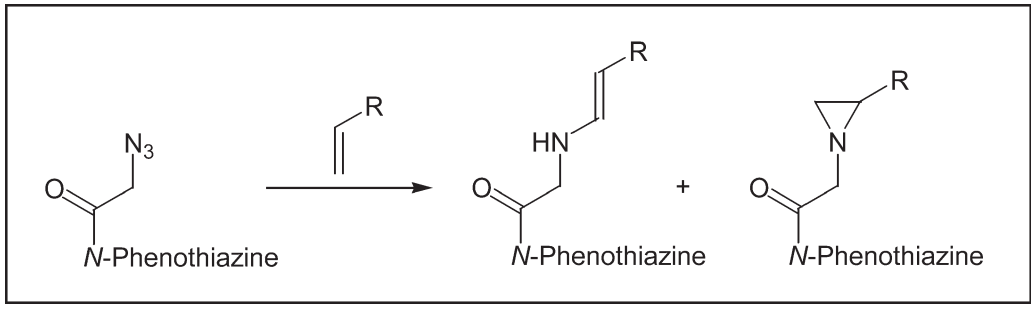


The reaction of 10-azidoacetyl-10*H*-phenothiazine with olefinic dipolarophiles depends on the reaction temperature. In refluxing toluene, a mixture of enamine and aziridine is formed in 3:1 ratio. The reaction mechanism appears to involve a Michael-type addition of the nucleophilic $N^1$ azide atom to the olefinic double bond. In chloroform, a cycloaddition reaction takes place with the formation of a 4,5-dihydro-1,2,3-triazole. The heating of dihydrotriazoles in toluene is accompanied by nitrogen elimination leading to a mixture of enamine and aziridine in 1:3 ratio.

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## INTRODUCTION

Phenothiazines and related compounds have shown diverse biological activities, *e.g.*, as tranquilizers [1], antimalarial [2], antipsychotropic [3], antimicrobial [4], antitubercular [5–7], or antitumor agents [8–10], reversers of multidrug resistance and potential activity in treatment of Alzheimer's and Creutzfeldt-Jakob diseases [11,12]. A slight variation in the substitution pattern of the phenothiazine often causes a marked difference in activities and therefore phenothiazines with various substituents are being synthesized and tested for activities in search of better medicinal agents. An important modification of the parent phenothiazine structure is the introduction of a substituent at the thiazine nitrogen atom. This substituent may contain an azide moiety, a grouping that leads to energy-rich and flexible intermediates and has enjoyed considerable interest since its discovery in 1864 [13–16]. Industrial interest in organic azide compounds began with the use of azides for the synthesis of heterocycles such as triazoles and tetrazoles, and other applications include use as blowing agents and as functional groups in pharmaceuticals.

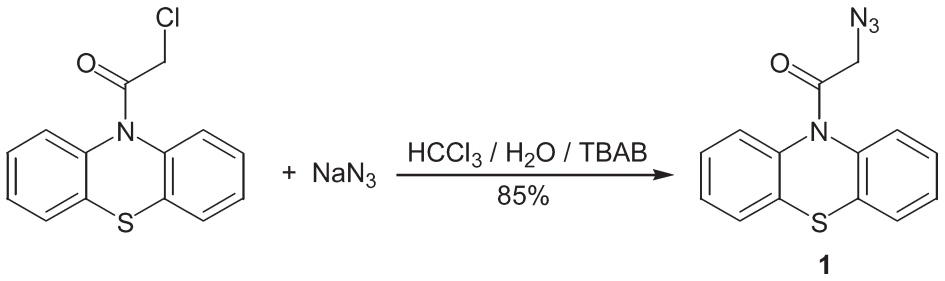
Azides can react very differently under different reaction conditions [17–19]. In principle, they react with electron-deficient compounds at $N^1$ [20–24] and electron-rich compounds at $N^3$ [25–28]. There can be not only retention of the azide unit but also cleavage of the nitrogen—nitrogen single bond, as in the case of nitrene chemistry [29–32]. The mechanistically simplest case, addition, has been extensively used in cycloaddition reactions. The Huisgen reaction of dipoles to dipolarophiles has been successfully applied with azides as dipoles [33].

## RESULTS AND DISCUSSION

Following our interest for the synthesis of new phenothiazine derivatives with biological activities, we report here the chemical behavior of 10-azidoacetyl-10*H*-phenothiazine **1** toward olefinic dipolarophiles. Compound **1** was obtained from 10-chloroacetyl-10*H*-phenothiazine [34] and sodium azide using tetrabutylammonium bromide as phase-transfer catalyst (Scheme 1).

Among dipolarophiles, terminal olefines and *N*-substituted maleinimides were used. The uncatalyzed thermal cycloaddition of azide **1** to acrylonitrile and ethyl acrylate allows the synthesis of 4,5-dihydro-1,2,3-triazoles **2a,b** (Scheme 2). The structure of triazoles **2a,b** has been proved by mass spectrometry and nuclear magnetic resonance (NMR) analysis. As expected, the reactions with terminal alkenes took place slowly, even in boiling chloroform. To shorten the reaction time, we decided to

**Scheme 1**




increase the reaction temperature up to the boiling point of toluene. Surprisingly, thin-layer chromatography monitoring of the reaction progress did not reveal a shorter reaction time. However, the reaction output was completely different, a mixture of enamine **3** and aziridine **4** being obtained in a ratio of 3:1 and total yield of 80% (Scheme 2, path ''a" and Table 1). For both compounds, mass spectrometric analysis showed molecular ions of *m*/*z* with 28 amu less than that in the corresponding triazoles. Nitrogen elimination was also indicated by the IR spectra of the enamine, which showed an intense absorption characteristic of a nitrogen—hydrogen bond (3349 $cm^{-1}$). The coupling constants of the vinylic hydrogens (13.8 Hz) indicated a selective synthesis of the *trans*-enamine.

Detailed structural information was obtained from X-ray analysis of **3a** (Fig. 1) and **4a** (Fig. 2). From the mechanistic point of view, we may assume that formation of enamine and aziridine takes place by thermal decomposition of 4,5-dihydro-1,2,3-triazole **2**. To check this assumption, the triazoles were heated in toluene for 36 h (Scheme 2, path ''b''). Although the same compounds were identified in the reaction mixture, the ratio of enamine and aziridine is 1 : 3 (Table 1), which is in sharp contrast to the ratio obtained through pathway ''a.'' The structure of aziridines obtained *via* pathway ''b'' was proved to be identical with those reported above.

The uncatalyzed thermal cycloaddition of azide **1** to *N*-substituted maleinimides proceeds in a similar manner to that described above. Thus, in chloroform, the

**Scheme 2**

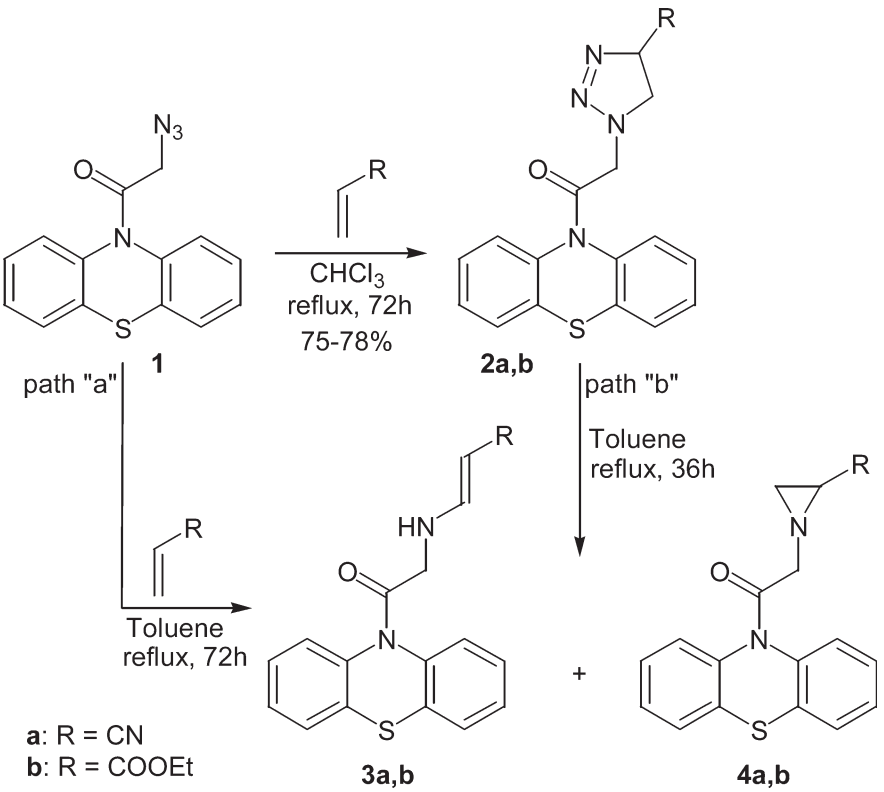


**Table 1**
Products ratio and total isolated yields.

| Compounds | Method | Ratio | Yield |
|---|---|---|---|
| **3a** + **4a** | Path a | 3:1 | 80 |
| **3b** + **4b** | Path a | 3:1 | 81 |
| **6a** + **7a** | Path a | 2.8:1 | 70 |
| **6b** + **7b** | Path a | 2.8:1 | 72 |
| **3a** + **4a** | Path b | 1:3 | 85 |
| **3b** + **4b** | Path b | 1:3 | 88 |
| **6a** + **7a** | Path b | 1:3 | 92 |
| **6b** + **7b** | Path b | 1:3 | 90 |

corresponding fused 4,5-dihydro-1,2,3-triazoles **5a,b** have been obtained in 80% isolated yield (Scheme 3). The structure of these compounds has been confirmed by mass spectrometry (MS) and NMR analysis.

The latter has revealed a coupling constant of 11 Hz for the *syn*-vicinal hydrogen atoms of the fused bridge. By changing the temperature to the boiling point of toluene, a mixture of enamine **6** and aziridine derivative **7** have been obtained in 70% total isolated yield (Scheme 3, path ''a''). As described in Table 1, the ratio of enamine and aziridine is again ca. 3 : 1. The formation of enamines **6** has been confirmed by the IR spectra which revealed a strong absorption band at 3319 $cm^{-1}$ for N—H bond. Both structures have been fully characterized by mass spectrometry and NMR analysis.

Thermal decomposition of 4,5-dihydro-1,2,3-triazoles **5** (Scheme 3, path ''b'') has provided again a mixture of enamine and aziridine derivative with the latter as major compound (Table 1). These facts suggest two different mechanistic pathways for the formation of enamine/aziridine mixture. By controlling the reaction temperature the formation and subsequent thermal decomposition of 4,5-dihydro-1,2,3-triazole **2** was allowed (path b). Alternatively, in refluxing toluene, the 10-azidoacetyl-10*H*-phenothiazine **1** undergoes a Michael-type addition of

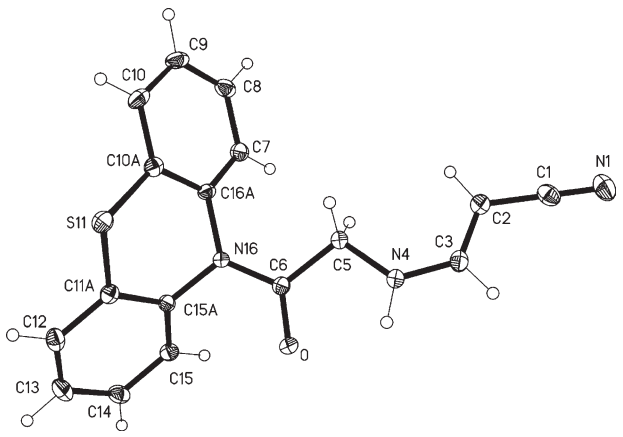



**Figure 1.** Molecular structure of enamine **3a**. Ellipsoids represent 50% probability levels.

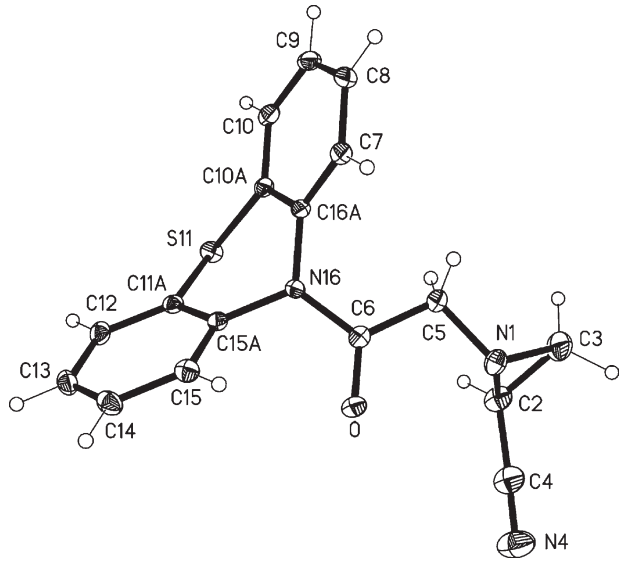



**Figure 2.** Molecular structure of aziridine **4a**. Ellipsoids represent 50% probability levels.

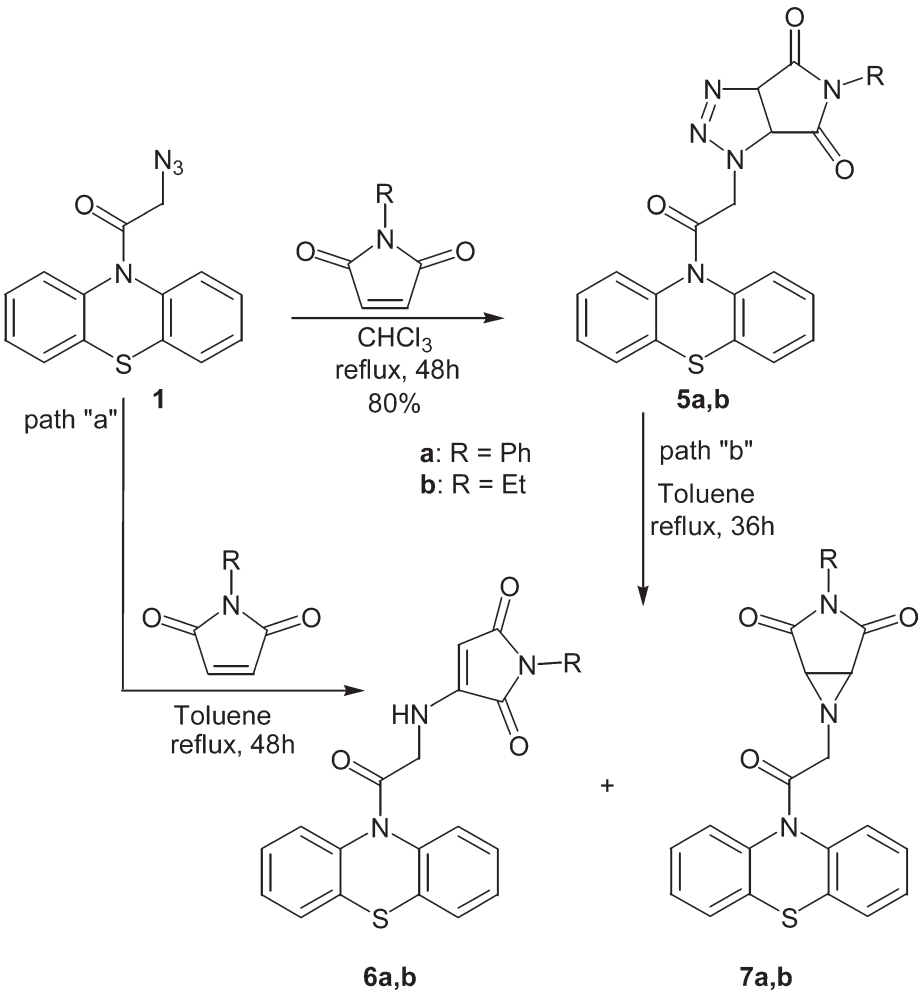
nucleophilic $N^1$ atom to the olefinic double bond (path ''a''). A simultaneous or subsequent elimination of molecular nitrogen opens the way for the aziridine ring closure or for a 1,2-hydride shift to the nitrogen atom. The latter process, which leads to the enamines **3**, appears to be favored. The formation of a nitrene compound before the Michael type interaction of azide with the olefinic dipolarophiles was ruled out by heating the azide **1** alone in toluene. Regardless of the concentration ($10^{-3}$ or 1*M*), after 72 h reflux, the azide was recovered in quantitative yields. Moreover, the prolonged heating of aziridines **4** and **7** in boiling toluene has ruled out their conversion to enamine compounds **3** and **6**.

In conclusion, we report here a temperature-dependent interaction between 10-azidoacetyl-10*H*-phenothiazine and olefinic dipolarophiles. In refluxing toluene, a mixture of enamine and aziridine is formed in 3:1 ratio. The reaction mechanism appears to involve a Michael type addition of nucleophilic $N^1$ azide atom to the olefinic double bond. In chloroform, a cycloaddition reaction takes place with the formation of a 4,5-dihydro-1,2,3-triazole. The heating of the 4,5-dihydro-1,2,3-triazoles in toluene is accompanied by nitrogen elimination leading to a mixture of enamine and aziridine in 1:3 ratio. It seems that by tuning the reaction temperature the selective synthesis of enamine or aziridine can be realized.

## EXPERIMENTAL

**General remarks.** Melting points: Büchi 510, uncorrected. IR: Bruker Tensor 27. $^1H$ and $^{13}C$ NMR: Bruker DRX 400 with tetramethylsilane as internal standard at room

**Scheme 3**




temperature. Chemical shifts are reported in ppm downfield from tetramethylsilane. MS: Finnigan MAT 90X, electron impact (EI). All reagents were commercially available and used without further purification.

**10-Azidoacetyl-10*H*-phenothiazine (1).** To a solution of 10-chloroacetyl-10*H*-phenothiazine (2.75 g, 10 mmol) in chloroform (30 mL) sodium azide (0.72 g, 11 mmol), water (15 mL), and tetrabutylammonium bromide (0.04 g, 0.12 mmol) were added. The reaction mixture was stirred vigorously at room temperature for 48 h and then separated. The organic layer was washed with water (3 × 20 mL), dried off ($Na_2SO_4$), and concentrated in vacuo. The residue was titrated with ethanol and the resulting solid recrystallized from ethanol (40 mL) to give **1** as colorless crystals; 2.4 g, 85%, mp 110–111°C; IR (attenuated total reflection [ATR]): 2105, 1682, 1459, 1367, 1253, 1178, 764 $cm^{-1}$; $^1$H-NMR ($CDCl_3$): δ 3.95 (bs, 2 H, $CH_2$), 7.21–7.50 (m, 8 H, 8 × $CH_{ar}$); $^{13}$C-NMR ($CDCl_3$): δ 50.9 (t), 126.6 (d), 127.3 (d), 127.4 (d), 128.2 (d), 133.0 (s), 137.5 (s), 166.7 (s); MS (EI): *m/z* (%) 282 (45) [$M^+$], 199 (100), 154 (12). Anal. Calcd. for $C_{14}H_{10}N_4OS$: C, 59.56; H, 3.57; N, 19.85. Found: C, 59.84; H, 3.68; N, 20.06.

**4,5-Dihydro-1,2,3-triazole 2a: Typical procedure.** A solution of **1** (1.41 g, 5 mmol) and acrylonitrile (0.33 mL, 5 mmol) in chloroform (30 mL) was heated under reflux for 72 h. The solvent was evaporated and the residue purified by column chromatography on silica gel with ethyl acetate : hexane 1 : 1 as eluent ($R_f$ = 0.35). Colorless crystals 1.3 g, 78%, mp 160–161°C; IR (ATR): 2103, 1664, 1458, 1381, 1260, 1115, 755, 735 $cm^{-1}$; $^1$H-NMR (dimethyl sulfoxide [DMSO]-$d_6$): δ 3.45 (dd, $^2J$ = 9.6, $^3J$ = 10 Hz, 1 H, H5), 3.58 (dd, $^2J$ = 9.6, $^3J$ = 12.4 Hz, 1 H, H5), 4.82 (bs, 2 H, $CH_2$), 5.52 (dd, $^3J$ = 10, 12.4 Hz, 1 H, H4), 7.32–7.75 (m, 8 H, 8 × $CH_{ar}$); $^{13}$C-NMR (DMSO-$d_6$): δ 48.4 (t), 50.4 (t), 63.7 (d), 117.1 (s), 127.1 (d), 127.4 (d), 128.0 (d), 132.1 (s), 137.3 (s), 166.3 (s); MS (EI): *m/z* (%) 335 (24) [$M^+$], 307 (72), 254 (8), 199 (100), 167 (20), 154 (18). Anal. Calcd. for $C_{17}H_{13}N_5OS$: C, 60.88; H, 3.91; N, 20.88. Found: C, 61.07; H, 4.14; N, 21.10.

**4,5-Dihydro-1,2,3-triazole 2b.** Following the typical procedure after 72 h reflux, compound **2b** ($R_f$ = 0.31) was obtained as colorless crystals; 1.43 g, 75%, mp 130–131°C. IR (ATR): 1736, 1680, 1462, 1299, 1104, 756 $cm^{-1}$; $^1$H-NMR ($CDCl_3$): δ 1.26 (t, $^3J$ = 7.2 Hz, 3 H, $CH_3$), 3.42 (dd, $^2J$ = 9.6, $^3J$ = 11 Hz, 1 H, H5), 3.55 (dd, $^2J$ = 9.6, $^3J$ = 12.4 Hz, 1 H, H5), 4.24 (q, $^3J$ = 7.2 Hz, 2 H, $OCH_2$), 4.90 (bs, 2 H, $CH_2$), 5.05 (dd, $^3J$ = 11, 12.4 Hz, 1 H, H4), 7.24–7.55 (m, 8 H, 8 × $CH_{ar}$); $^{13}$C-NMR ($CDCl_3$): δ 14.1 (q), 47.1 (t), 51.7 (t), 62.0

(t), 79.5 (d), 126.7 (d), 126.9 (d), 127.2 (d), 127.3 (d), 127.4 (d), 128.1 (d), 128.2 (d), 133.0 (s), 137.5 (s), 137.6 (s), 166.6 (s), 168.2 (s); MS (EI): *m/z* (%) = 382 (14) [$M^+$], 354 (79), 199 (100), 154 (24). Anal. Calcd. for $C_{19}H_{18}N_4O_3S$: C, 59.67; H, 4.74; N, 14.65. Found: C, 59.88; H, 4.55; N, 14.81.

**4,5-Dihydro-1,2,3-triazole 5a.** Following the typical procedure after 48 h reflux, compound **5a** ($R_f = 0.26$) was obtained as colorless crystals; 1.82 g, 80%, mp 180–181°C. IR (ATR): 1715, 1712, 1459, 1384, 1256, 1183, 765, 692 $cm^{-1}$; $^1$H-NMR (DMSO-$d_6$): δ 4.55 (d, $^3J$ = 11 Hz, 1 H, CH), 5.02 (bs, 2 H, $CH_2$), 5.81 (d, $^3J$ = 11 Hz, 1 H, CH), 7.12 (m, 2 H, 2 × $CH_{ar}$), 7.39 (m, 7 H, 7 × $CH_{ar}$), 7.60 (m, 2 H, 2 × $CH_{ar}$), 7.73 (m, 2 H, 2 × $CH_{ar}$); $^{13}$C-NMR (DMSO-$d_6$): δ 49.4 (t), 57.2 (d), 82.8 (d), 126.6 (d), 126.9 (s), 127.1 (s), 127.5 (d), 128.0 (d), 128.6 (d), 128.8 (d), 131.5 (s), 132.1 (s), 137.0 (s), 167.1 (s), 170.5 (s), 171.8 (s); MS (EI): *m/z* (%) 455 (15) [$M^+$], 427 (85), 350 (34), 199 (100), 154 (25). Anal. Calcd for $C_{24}H_{17}N_5O_3S$: C, 63.29; H, 3.76; N, 15.38. Found: C, 63.51; H, 3.82; N, 15.62.

**4,5-Dihydro-1,2,3-triazole 5b.** Following the typical procedure after 48 h reflux, compound **5b** ($R_f = 0.26$) was obtained as colorless crystals; 1.63 g, 80%, mp 167–168°C. IR (ATR): 1705, 1682, 1462, 1395, 1257, 1223, 1131, 752, 598 $cm^{-1}$; $^1$H NMR (DMSO-$d_6$): δ 0.97 (t, $^3J$ = 7.1 Hz, 3 H, $CH_3$), 3.37 (q, $^3J$ = 7.1 Hz, 2 H, $OCH_2$), 4.40 (d, $^3J$ = 10.6 Hz, 1 H, CH), 4.75 (bs, 1 H, $CH_2$), 5.01 (bs, 1 H, $CH_2$), 5.63 (d, $^3J$ = 10.6 Hz, 1 H, CH), 7.34–7.73 (m, 8 H, 8 × $CH_{ar}$); $^{13}$C NMR (DMSO-$d_6$): δ = 12.1 (q), 33.3 (t), 49.5 (t), 57.4 (d), 82.7 (d), 126.9 (d), 127.3 (d), 127.9 (d), 132.0 (s), 137.1 (s), 166.4 (s), 170.9 (s), 172.4 (s); MS (EI): *m/z* (%) = 407 (18) [$M^+$], 379 (57), 352 (28), 199 (100), 154 (28). Anal. Calcd. for $C_{20}H_{17}N_5O_3S$: C, 58.96; H, 4.21; N, 17.19. Found: C, 59.12; H, 4.38; N, 17.43.

**Enamine 3a and aziridine 4a: Path "a"—Typical procedure.** A solution of **1** (1.41 g, 5 mmol) and acrylonitrile (0.33 mL, 5 mmol) in toluene (30 mL) was heated under reflux for 72 h. The solvent was evaporated and the residue purified by column chromatography on silica gel with ethyl acetate : hexane 1 : 1 as eluent.

***Enamine 3a.*** Colorless crystals 0.92 g, 60%, mp 194–195°C, $R_f$ =0.3. IR (ATR): 3349, 2191, 1672, 1624, 1441, 1384, 1258, 766, 748, 602 $cm^{-1}$; $^1$H-NMR ($CDCl_3$): δ 3.68 (d, $^3J$ = 13.8, 1 H, CH), 3.78 (bs, 2 H, $CH_2$), 5.67 (m, 1 H, NH), 7.00 (dd, $^3J$ = 7.1, 13.8 Hz, 1 H, CH), 7.27–7.56 (m, 8 H, 8 × $CH_{ar}$); $^{13}$C-NMR ($CDCl_3$): δ = 44.9 (t), 63.3 (d), 120.9 (s), 126.5 (d), 127.4 (d), 127.8 (d), 128.4 (d), 133.0 (s), 149.4 (d), 166.8 (s); MS (EI): *m/z* (%) 307 (29) [$M^+$], 199 (100), 198 (76), 167 (21), 154 (15). Anal. Calcd. for $C_{17}H_{13}N_3OS$: C, 66.43; H, 4.26; N, 13.67. Found: C, 66.51; H, 4.47; N, 13.82.

***Aziridine 4a.*** Colorless crystals 0.3 g, 20%, mp 177–178°C, $R_f$ =0.24. IR (ATR): 2245, 1684, 1460, 1378, 1258, 1183, 754, 655 $cm^{-1}$; $^1$H-NMR (DMSO-$d_6$): δ 1.89 (d, $^3J$ = 6.4 Hz, 1 H, $CH_2$), 2.25 (d, $^3J$ = 3.2 Hz, 1 H, $CH_2$), 2.61 (dd, $^3J$ = 3.2, 6.4 Hz, 1 H, CH), 3.28 (bs, 1 H, $CH_2$), 3.42 (bs, 1 H, $CH_2$), 7.31–7.64 (m, 8 H, 8 × $CH_{ar}$); $^{13}$C-NMR (DMSO-$d_6$): δ = 22.7 (d), 33.1 (t), 59.2 (t), 119.5 (s), 127.1 (s), 127.3 (s), 127.4 (d), 128.0 (d), 132.2 (s), 137.6 (s), 167.2 (s); MS (EI): *m/z* (%) 307 (27) [$M^+$], 199 (62), 198 (100), 167 (19), 154 (12). Anal. Calcd. for $C_{17}H_{13}N_3OS$: C, 66.43; H, 4.26; N, 13.67. Found: C, 66.56; H, 4.42; N, 13.76.

***Enamine 3b.*** Following the typical procedure after 72 h reflux, compound **3b** ($R_f = 0.28$) was obtained as colorless crystals: 1.07 g, 61%, mp 175–176°C. IR (ATR): 3358, 1696, 1671, 1608, 1148, 978, 760, 623 $cm^{-1}$; $^1$H-NMR ($CDCl_3$): δ 1.24 (t, $^3J$ = 6.4 Hz, 3 H, $CH_3$), 3.82 (bs, 2 H, $CH_2$), 4.11 (m, 3 H, $OCH_2$ + CH), 4.47 (d, $^3J$ = 12.8 Hz, 1 H, CH), 5.59 (bs, 1 H, NH), 7.29–7.57 (m, 8 H, 8 × $CH_{ar}$); $^{13}$C-NMR ($CDCl_3$): δ = 14.5 (q), 49.9 (t), 59.1 (t), 87.0 (d), 126.8 (d), 127.1 (d), 127.2 (s), 127.3 (d), 128.2 (d), 128.4 (d), 133.2 (s), 137.7 (s), 147.3 (d), 167.3 (s), 169.0 (s); MS (EI): *m/z* (%) 354 (11) [$M^+$], 309 (5), 199 (100), 167 (16). Anal. Calcd. for $C_{19}H_{18}N_2O_3S$: C, 64.39; H, 5.12; N, 7.90. Found: C, 64.58; H, 5.26; N, 8.12.

***Aziridine 4b.*** Following the typical procedure after 72 h reflux, compound **4b** ($R_f = 0.11$) was obtained as yellow crystals: 0.35 g, 20%, mp 107–108°C. IR (ATR): 1676, 1458, 1116, 766, 749, 657 $cm^{-1}$; $^1$H-NMR ($CDCl_3$): δ 1.24 (t, $^3J$ = 7.2 Hz, 3 H, $CH_3$), 2.14 (m, 1 H, CH), 3.52 (bs, 2 H, $CH_2$), 3.61 (m, 2 H, $CH_2$), 4.21 (q, $^3J$ = 7.2 Hz, 2 H, $OCH_2$), 7.22–7.58 (m, 8 H, 8 × $CH_{ar}$); $^{13}$C-NMR ($CDCl_3$): δ 14.5 (q), 44.1 (t), 50.0 (t), 60.75 (d), 60.8 (t), 126.9 (d), 127.1 (d), 128.1 (d), 133.2 (s), 138.0 (s), 166.8 (s), 170.3 (s); MS (EI): *m/z* (%) 354 (14) [$M^+$], 199 (100), 167 (24). Anal. Calcd. for $C_{19}H_{18}N_2O_3S$: C, 64.39; H, 5.12; N, 7.90. Found: C, 64.64; H, 5.31; N, 8.14.

***Enamine 6a.*** Following the typical procedure after 48 h reflux compound **6a** ($R_f = 0.41$) was obtained as yellow crystals: 1.1 g, 51%, mp 193–194°C. IR (ATR): 3318, 1704, 1686, 1636, 1388, 1178, 767 $cm^{-1}$; $^1$H-NMR ($CDCl_3$): δ 4.01 (bs, 2 H, $CH_2$), 4.83 (s, 1 H, CH), 6.34 (bs, 1 H, NH), 7.20–7.58 (m, 13 H, 13 × $CH_{ar}$); $^{13}$C-NMR ($CDCl_3$): δ 45.9 (t), 86.2 (d), 125.8 (d), 126.4 (d), 126.6 (d), 127.2 (d), 127.3 (d), 127.4 (d), 127.8 (d), 128.0 (d), 128.4 (d), 128.5 (d), 128.8 (d), 129.0 (d), 129.1 (d), 131.7 (s), 137.0 (s), 137.6 (s), 147.9 (s), 165.6 (s), 166.1 (s), 170.3 (s); MS (EI): *m/z* (%) = 427 (34) [$M^+$], 350 (35), 199 (100). Anal. Calcd. for $C_{24}H_{17}N_3O_3S$: C, 67.43; H, 4.01; N, 9.83. Found: C, 67.61; H, 4.21; N, 10.12.

***Aziridine 7a.*** Following the typical procedure after 48 h reflux compound **7a** ($R_f = 0.33$) was obtained as yellow pale crystals: 0.39 g, 19%, mp 196–197°C. IR (ATR): 1718, 1687, 1461, 1362, 1181, 765, 749, 693 $cm^{-1}$; $^1$H-NMR ($CDCl_3$): δ 4.59 (d, $^3J$ = 11.2 Hz, 1 H, CH), 5.03 (bs, 2 H, $CH_2$), 5.74 (d, $^3J$ = 11.2 Hz, 1 H, CH), 7.17–7.57 (m, 13 H, 13 × $CH_{ar}$); $^{13}$C-NMR ($CDCl_3$): δ 50.1 (t), 57.3 (d), 82.8 (d), 125.8 (d), 126.3 (d), 126.7 (d), 127.2 (d), 127.5 (d), 128.2 (d), 128.9 (d), 129.0 (d), 129.2 (d), 130.8 (s), 137.0 (s), 167.0 (s), 169.2 (s), 171.5 (s); MS (EI): *m/z* (%) 427 (31) [$M^+$], 350 (25), 199 (100). Anal. Calcd. for $C_{24}H_{17}N_3O_3S$: C, 67.43; H, 4.01; N, 9.83. Found: C, 67.68; H, 4.18; N, 10.08.

***Enamine 6b.*** Following the typical procedure after 48 h reflux compound **6b** ($R_f = 0.4$) was obtained as yellow pale crystals: 1.0 g, 53%, mp 178–179°C. IR (ATR): 3319, 1706, 1684, 1392, 1175, 760 $cm^{-1}$; $^1$H-NMR ($CDCl_3$): δ 0.99 (t, $^3J$ = 6.9 Hz, 3 H, $CH_3$), 3.34 (q, $^3J$ = 6.9 Hz, 2 H, $OCH_2$), 4.11 (bs, 2 H, $CH_2$), 4.80 (s, 1 H, CH), 6.11 (bs, 1 H, NH), 7.24–7.53 (m, 8 H, 8 × $CH_{ar}$); $^{13}$C-NMR ($CDCl_3$): δ 12.0 (q), 33.1 (t), 46.2 (t), 87.5 (d), 126.8 (d), 127.4 (d), 127.9 (d), 132.1 (s), 137.3 (s), 165.7 (s), 166.5 (s), 170.1 (s); MS (EI): *m/z* (%) 379 (61) [$M^+$], 350 (35), 199 (100). Anal. Calcd. for $C_{20}H_{17}N_3O_3S$: C, 63.31; H, 4.52; N, 11.07. Found: C, 63.57; H, 4.78; N, 11.33.

***Aziridine 7b.*** Following the typical procedure after 48 h reflux, compound **7b** ($R_f = 0.3$) was obtained as yellow pale crystals: 0.36 g, 19%, mp 185–186°C. IR (ATR): 1711, 1684, 1461, 1374, 1154, 760, 691 $cm^{-1}$; $^1$H-NMR ($CDCl_3$): δ 0.98 (t, $^3J = 6.9$ Hz, 3 H, $CH_3$), 3.30 (q, $^3J = 6.9$ Hz, 2 H, $OCH_2$), 4.51 (d, $^3J = 11.2$ Hz, 1 H, CH), 4.98 (bs, 2 H, $CH_2$), 5.72 (d, $^3J = 11.2$ Hz, 1 H, CH), 7.19–7.48 (m, 8 H, 8 × $CH_{ar}$); $^{13}$C-NMR ($CDCl_3$): δ 12.5 (q), 32.8 (t), 49.8 (t), 57.1 (d), 82.3 (d), 126.9 (d), 127.5 (d), 127.9 (d), 132.4 (s), 137.2 (s), 167.1 (s), 169.5 (s), 171.8 (s); MS (EI): *m/z* (%) 379 (45) [$M^+$], 350 (31), 199 (100). Anal. Calcd. for $C_{20}H_{17}N_3O_3S$: C, 63.31; H, 4.52; N, 11.07. Found: C, 63.55; H, 4.81; N, 11.29.

**Enamines and aziridines: Path "b"—Typical procedure.** A solution of 4,5-dihydro-1,2,3-triazole (1 mmol) in toluene (30 mL) was heated at reflux for 36 h. The solvent was evaporated and the residue purified by column chromatography on silica gel with ethyl acetate:hexane 1:1 as eluent. Products ratio and total yields are described in Table 1.

***Crystal structure determination of 3a.*** Crystal data: monoclinic, space group $P2_1/n$, $a = 12.4076(3)$, $b = 8.8927(2)$, $c = 13.7600(3)$ Å, $\beta = 105.076(3)°$, $Z = 4$, $T = 100(2)$ K. Data collection: a crystal ca. 0.3 × 0.25 × 0.1 $mm^3$ was used to record 44,648 intensities on a Oxford Diffraction Xcalibur E diffractometer using Mo Kα radiation ($\lambda = 0.71073$ Å). Structure refinement: the structure was refined anisotropically on $F^2$ (program SHELXL-97 [35]) to $wR2 = 0.0856$, $R1 = 0.0308$ for 203 parameters and 4254 unique reflexions. The NH hydrogen was refined freely, other hydrogens using a riding model. Data have been deposited in Cambridge under the number CCDC-753518.

***Crystal structure determination of 4a.*** Crystal data: monoclinic, space group $P2_1/c$, $a = 12.6700(3)$, $b = 8.4297(2)$, $c = 13.7418(3)$ Å, $\beta = 91.868(3)°$, $Z = 4$, $T = 100(2)$ K. Data collection: a crystal ca. 0.3 × 0.2 × 0.1 $mm^3$ was used to record 52,950 intensities as above. Structure refinement: the structure was refined as above to $wR2 = 0.0869$, $R1 = 0.0305$ for 211 parameters and 4364 unique reflexions. The aziridine hydrogens were refined freely, other hydrogens using a riding model. Data have been deposited in Cambridge under the number CCDC-753519.

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