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SYNTHESIS OF 1,2,4-TRIAZOLO[3,2-*b*]BENZOTHIAZOLES BY PHOTOLYSIS OF SULFILIMINES HAVING A (METHYLTHIO)CARBONIMIDOYL GROUP

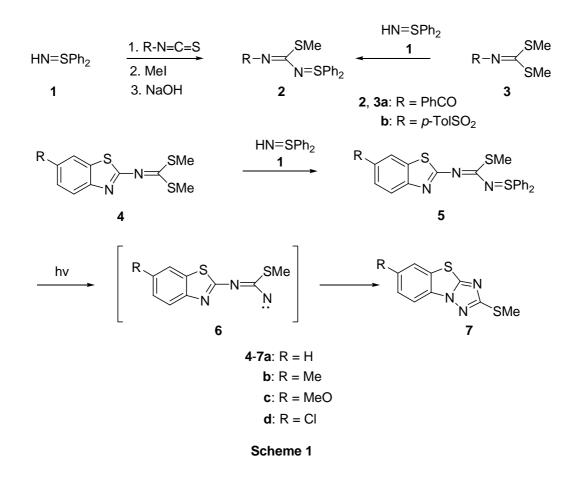
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Abstract – The reaction of dimethyl N-(2-benzothiazolyl)dithiocarbonimidates(4) with N-unsubstituted S,S-diphenylsulfilimine(1) gaveN-[N-(2-benzothiazolyl)methylthiocarbonimidoyl]-S,S-diphenylsulfilimines(5),which were cyclized by phtolysis to 1,2,4-triazolo[3,2-b]benzothiazoles (7).

In our preceding papers¹ we have shown that *N*-(3-oxopropenyl)sulfilimines (R-CO-C=C-N=SPh₂) were readily prepared by a substitution reaction using *N*-unsubstituted sulfilimines (**1**) and that they served as useful building blocks for heterocycle synthesis. In our continuous study on conjugated sulfilimines, we became interested in new synthesis of sulfilimines conjugated with a carbon-nitrogen double bond (R-N=C-N=SR'₂) and their reactions. A variety of sulfilimines conjugated with a carbon-nitrogen double bond have been prepared: *N*-(*N*-arylimidoyl)sulfilimines (Ar-N=CPh-N=SMe₂) were obtained by the substitution reaction of carbonimidoyl halides (Ar-N=CCl-Ph) with *N*-unsubsituted sulfilimines² and by base treatment of salts (Ar-N=CPh-NH-S⁺Me₂Cl⁻) obtained from *N*-chlorobenzamidine and dimethyl sulfide.³ Furthermore, the reaction of *N*-thiocarbamoylsulfilimines (Ar-NH-CS-N=SPh₂), obtained by addition of **1** to aryl isothiocyanates, with iodomethane followed by base treatment resulted in the formation of *N*-[(methylthio)carbonimidoyl]sulfilimines (**2**) (Scheme 1).⁴ However, in the synthesis of **2**, the availability of the starting aryl isothiocyanate is rather limited. Therefore, we studied the preparation of these sulfilimines from more readily available materials, *e. g.*, dimethyl carbondithioimidate (**3**), which are readily prepared from the corresponding amines, carbon disulfide, and iodomethane in the presence of a base.⁵

The reaction of dimethyl *N*-benzoyldithiocarbonimidate $(3a)^6$ with 1 in acetonitrile at room temperature gave the expected sulfilimine (2a) in 62% yield. *N*-(*p*-Tolylsulfonyl) derivative (2b) was obtained in



79% yield by similar treatment of dimethyl *N*-(*p*-tolylsulfonyl)dithiocarbonimidate (**3b**).⁷

It has been reported that the reaction of 2 (R=Me, Ph) with carbon disulfide gave isothiocyanates R-NCS, nitrile R-CN, diphenyl sulfide, and elemental sulfur.⁴ However, no further synthetic utility of **2** has been In order to develop the utility of this type of sulfilimine for heterocycle synthesis, shown. N-(2-benzothiazolyl) derivative (5) was chosen and its photolysis and thermolysis were studied. The reaction of carbondithioimidates $(4a-d)^8$ of commercially available 2-aminobenzothiazoles with 1 in acetonitrile at room temperature for N-[None dav gave (2-benzothiazolyl)methylthiocarbonimidoyl]sulfilimines (5a-d) in 53-85% yields. Since these compounds have a 1,3-diazabutadienyl system conjugated with sulfilimine, N=C-N=C-N=SPh₂, it would be possible to cyclize to 1,2,4-triazole by photolysis or thermolysis on extrusion of diphenyl sulfide. Attempted thermolysis of 5a in refluxing toluene resulted in the formation of an intractable tar. However, photolysis of 5a gave а product whose structure was assigned as 2-methylthio-1,2,4-triazolo[3,2-b] benzothiazole (7a) on the basis of spectral and analytical data. The best yield of 7a was a 62% yield when a solution of 5a in ethyl acetate was irradiated by a high-pressure mercury lamp under a nitrogen atmosphere for 30 minutes and then the product was purified by column chromatography. Other products (7b-d) were similarly obtained in 51-82% yields.

The reaction would proceed *via* formation of a nitrene intermediate (**6**) followed by 6π -electrocyclization to 1,2,4-triazolo[3,2-*b*]benzothiazoles through radical or nitrene intermediates has been reported in the pyrolysis of 1-(2-benzothiazolyl)-2-aryl-1,2,3,4-tetrazoles, where nitrogen was extruded from the tetrazole ring to generate the intermediate.⁹ On the other hand, 1,3-thiaza-allyl radical intermediates were proposed in the formation of [1,3]thiazolo[3,2-*b*]-1,2,4-triazole by gas-phase pyrolysis of 4-amino-3-allylthio-1,2,4-triazoles.¹⁰ Similar cyclization of a N=C-N=C-N=SPh₂ system to 1,2,4-triazole was previously observed in the limited case of thermolysis and photolysis of *S*,*S*-dimethyl-*N*-[*N*-(2-pyridyl)benzimidoyl]sulfilimine to 2-phenyl-1,2,4-triazolo[1,5-*a*]pyridine.²

We have developed a simple method for synthesis of *N*-(methylthiocarbonimidoyl)sulfilimines, R-N=C(SMe)N=SPh₂, and a photochemical transformation of their conjugated system, (2-benzothiazolyl)-N=C(SMe)-N=SPh₂, giving 1,2,4-triazolo[3,2-*b*]benzothiazoles.

EXPERIMENTAL

All Melting points were determined with MRK MEL-TEMP II and are uncorrected. The IR spectra were measured on a JASCO FT/IR-420 spectrophotometer. MS and NMR spectra were taken with JEOL JMS DX-300 and JEOL GSX-400, respectively. Microanalysis were performed with YANACO CHN-CODER MT-5.

N-[(*N*-Benzoyl)methylthiocarbonimidoyl)]-*S*,*S*-diphenylsulfilimine (2a).

A mixture of **3a** (225 mg, 1.0 mmol) and **1** (242 mg, 1.2 mmol) in MeCN (5 mL) was stirred at rt for 4 h. The precipitates formed were collected by filtration and recrystallized from MeCN to give **2a** (235 mg, 62%), white needles, mp 122 °C (decomp). IR (KBr): 1604, 1570, 1446, 1414, 1346 cm⁻¹. ¹H-NMR (CDCl₃): δ 2.64 (s, 3H, SMe), 7.28-8.01 (m, 15H, ArH). *Anal*. Calcd for C₂₁H₁₈N₂OS₂: C, 66.64; H, 4.79; N, 7.40. Found: C, 66.70; H, 4.97; N, 7.48.

S,S-Diphenyl-N-[(N-p-toluenesulfonyl)methylthiocarbonimidoyl]sulfilimine (2b).

A mixture of **3b** (688 mg, 2.5 mmol) and **1** (1.01 g, 5.0 mmol) in MeCN (5 mL) was stirred at rt for 1 day. The precipitates formed were collected by filtration to give **2b** (848 mg, 79%), white prisms, mp 122-124 °C (MeCN). IR (KBr): 1423, 1281, 1147, 1088, 966 cm⁻¹. ¹H-NMR (CDCl₃): δ 2.35 (s, 3H, Me), 2.56 (s, 3H, Me), 7.08-7.68 (m, 14H, ArH). *Anal*. Calcd for C₂₁H₂₀N₂O₂S₃: C, 58.85, H, 4.70; N, 6.54. Found: C, 58.97; H, 4.75; N, 6.63.

N-[*N*-(2-Benzothiazolyl)methylthiocarbonimidoyl]-*S*,*S*-diphenylsulfilimine (5a). Typical experimental procedure:

A mixture of **4a** (254 mg, 1.0 mmol) and **1** (201 mg, 1.0 mmol) in MeCN (5 mL) was stirred at rt for 1 day. The precipitates formed were collected by filtration and recrystallized from MeCN to give **5a** (237 mg, 58%), white prisms, mp 139-142 °C. IR (KBr): 1485, 1439, 1415, 1323, 1261, 1140 cm⁻¹. ¹H-NMR (DMSO-*d*₆): δ 2.63 (s, 3H, Me), 7.13-7.99 (m, 14H, ArH). *Anal.* Calcd for C₂₁H₁₇N₃S₃: C, 61.88; H, 4.20; N, 10.31. Found: C, 61.66; H, 4.33; N, 10.14.

N-[*N*-(6-Methylbenzothiazol-2-yl)methylthiocarbonimidoyl]-*S*,*S*-diphenylsulfilimine (5b).

Yellow powders (53%), mp 108-111 °C (MeCN). IR (KBr): 1491, 1454, 1427, 1319, 1271, 1242, 1140 cm⁻¹. ¹H-NMR (CDCl₃): δ 2.40 (s, 3H, C6-Me), 2.67(s, 3H, SMe), 7.09-7.82 (m, 13H, ArH). *Anal.* Calcd for C₂₂H₁₉N₃S₃: C, 62.67; H, 4.54; N, 9.97. Found: C, 62.55; H, 4.56; N, 10.15.

N-[*N*-(6-Methoxylbenzothiazol-2-yl)methylthiocarbonimidoyl]-*S*,*S*-diphenylsulfilimine (5c).

Yellow powders (61%), mp 118-120 °C (MeCN). IR (KBr): 1599, 1493, 1450, 1427, 1269, 1209, 1063 cm⁻¹. ¹H-NMR (CDCl₃): δ 2.69 (s, 3H, SMe), 3.82 (s, 3H, OMe), 6.89-7.82 (m, 13H, ArH). *Anal.* Calcd for C₂₂H₁₉N₃OS₃: C, 60.38; H, 4.38; N, 9.60. Found: C, 60.39; H, 4.38; N, 9.75.

N-[N-(6-Chlorobenzothiazol-2-yl) methylthiocarbonimidoyl]-S, S-diphenyl sulfilimine (5d).

Yellow powders (84%), mp 125-126 °C (MeCN). IR (KBr): 1587, 1489, 1439, 1392, 1323, 1255 cm⁻¹. ¹H-NMR (CDCl₃): δ 2.68 (s, 3H, SMe), 7.23-7.82 (m, 13H, ArH). *Anal.* Calcd for C₂₁H₁₆ClN₃S₃: C, 57.06; H, 3.65; N, 9.51. Found: C, 57.04; H, 3.70; N, 9.66.

2-Methylthio-1,2,4-triazolo[3,2-b]benzothiazole (7a). Typical experimental procedure:

A solution of **5a** (408 mg, 1.0 mmole) in EtOAc (200 mL) was irradiated by a high pressure mercury lamp for 30 minutes under a nitrogen atmosphere. After evaporation of the solvent *in vacuo*., the black residue was purified by column chromatography on silica gel with CHCl₃ to give **7a** (138 mg, 62%), white needles, mp 104-105 °C (MeOH). IR (KBr): 1479, 1442, 1389, 1333, 1244 cm⁻¹. ¹H-NMR (CDCl₃): δ 2.71 (s, 3H, SMe), 7.35-7.91 (m, 4H, ArH). MS: m/z (%) 221 (M⁺, 100), 206 (77), 175 (77), 150 (71), 102 (88). *Anal.* Calcd for C₉H₇N₃S₂: C, 48.85; H, 3.19; N, 18.99. Found: C, 48.78; H, 3.31; N, 19.20.

6-Methyl-2-methylthio-1,2,4-triazolo[3,2-b]benzothiazole (7b).

White needles (59%), mp 129-130 °C (MeOH). IR (KBr): 1489, 1450, 1248 cm⁻¹. ¹H-NMR (CDCl₃): 2.49 (s, 3H, C6-Me), 2.70 (s, 3H, SMe), 7.31-7.78 (m, 3H, ArH). MS: m/z (%) 235 (M⁺, 100), 202 (39), 188 (68), 164 (44), 121 (31), 102 (44). *Anal*. Calcd for $C_{10}H_9N_3S_2$: C, 51.03; H, 3.85; N, 17.86. Found: C, 51.01; H, 3.81; N, 18.05.

6-Methoxy-2-methylthio-1,2,4-triazolo[3,2-b]benzothiazole (7c).

White needles (82%), mp 152-153 °C (MeOH). IR (KBr): 1493, 1448, 1309, 1232, 1026 cm⁻¹. ¹H-NMR (CDCl₃): δ 2.70 (s, 3H, SMe), 3.89 (s, 3H, OMe), 7.02-7.80 (m, 3H, ArH). MS: m/z (%) 251 (M⁺, 90), 218 (24), 204 (100), 190 (32), 181 (15), 102 (27). *Anal.* Calcd for C₁₀H₉N₃OS₂: C, 47.78, H, 3.61; N, 16.72. Found: C, 47.77; H, 3.60; N, 16.81.

6-Chloro-2-methylthio-1,2,4-triazolo[3,2-b]benzothiazole (7d).

White needles (51%), mp 156-157 °C (MeOH). IR (KBr): 1479, 1448, 1242 cm⁻¹. ¹H-NMR (CDCl₃): δ 2.70 (s, 3H, SMe), 7.49-7.83 (m, 3H, ArH). MS: m/z (%) 257 (M⁺+2, 32), 255 (M⁺, 36), 210 (47), 197 (28), 184 (100), 136 (24). *Anal*. Calcd for C₉H₆ClN₃S₂: C, 42.26; H, 2.36; N, 16.43. Found: C, 42.30; H, 2.51; N, 16.61.

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