HETEROCYCLES, Vol. 71, No. 6, 2007, pp. 1407 - 1411. © The Japan Institute of Heterocyclic Chemistry
Received, 1st March, 2007, Accepted, 16th April, 2007, Published online, 17th April, 2007. COM-07-11043

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

Masahiko Takahashi* and Shohtaroh Satoh

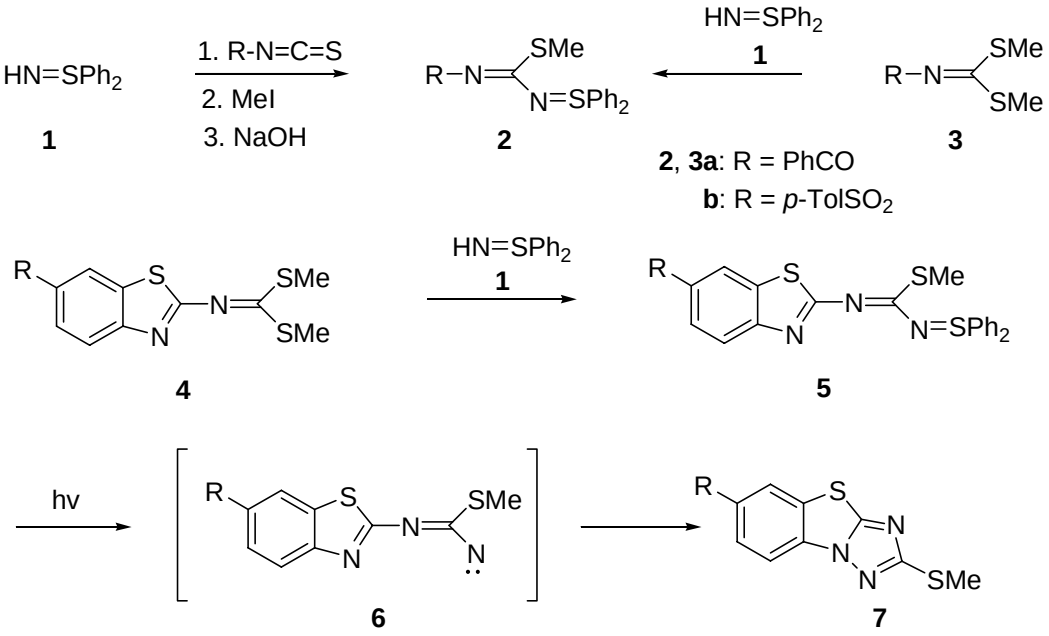
Department of Materials Science, Faculty of Engineering, Ibaraki University, Hitachi, Ibaraki 316-8511, Japan

Abstract – The reaction of dimethyl *N*-(2-benzothiazolyl)dithiocarbonimidates (**4**) with *N*-unsubstituted *S*,*S*-diphenylsulfilimine (**1**) gave *N*-[*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 papers[1] we have shown that *N*-(3-oxopropenyl)sulfilimines (R-CO-C=C-N=SPh_2) 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=SMe_2) were obtained by the substitution reaction of carbonimidoyl halides (Ar-N=CCl-Ph) with *N*-unsubsituted sulfilimines[2] and by base treatment of salts (Ar-N=CPh-NH-$S^+Me_2Cl^-$) obtained from *N*-chlorobenzamidine and dimethyl sulfide.[3] Furthermore, the reaction of *N*-thiocarbamoylsulfilimines (Ar-NH-CS-N=SPh_2), 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]



4-**7a**: R = H
b: R = Me
c: R = MeO
d: R = Cl

Scheme 1

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 shown. In order to develop the utility of this type of sulfilimine for heterocycle synthesis, *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 one day gave *N*-[*N*-(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=SPh_2, 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 a 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-triazole (**7**). Cyclization 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=SPh_2 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=SPh_2, and a photochemical transformation of their conjugated system, (2-benzothiazolyl)-N=C(SMe)-N=SPh_2, 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}. ^{1}H-NMR ($CDCl_3$): δ 2.64 (s, 3H, SMe), 7.28-8.01 (m, 15H, ArH). *Anal.* Calcd for $C_{21}H_{18}N_2OS_2$: 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}. ^{1}H-NMR ($CDCl_3$): δ 2.35 (s, 3H, Me), 2.56 (s, 3H, Me), 7.08-7.68 (m, 14H, ArH). *Anal*. Calcd for $C_{21}H_{20}N_2O_2S_3$: 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}. ^{1}H-NMR (DMSO-d_6): δ 2.63 (s, 3H, Me), 7.13-7.99 (m, 14H, ArH). *Anal*. Calcd for $C_{21}H_{17}N_3S_3$: 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}. ^{1}H-NMR ($CDCl_3$): δ 2.40 (s, 3H, C6-Me), 2.67(s, 3H, SMe), 7.09-7.82 (m, 13H, ArH). *Anal*. Calcd for $C_{22}H_{19}N_3S_3$: 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}. ^{1}H-NMR ($CDCl_3$): δ 2.69 (s, 3H, SMe), 3.82 (s, 3H, OMe), 6.89-7.82 (m, 13H, ArH). *Anal.* Calcd for $C_{22}H_{19}N_3OS_3$: 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*-diphenylsulfilimine (5d).**

Yellow powders (84%), mp 125-126 °C (MeCN). IR (KBr): 1587, 1489, 1439, 1392, 1323, 1255 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 2.68 (s, 3H, SMe), 7.23-7.82 (m, 13H, ArH). *Anal*. Calcd for $C_{21}H_{16}ClN_3S_3$: 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 $CHCl_3$ to give **7a** (138 mg, 62%), white needles, mp 104-105 °C (MeOH). IR (KBr): 1479, 1442, 1389, 1333, 1244 cm^{-1}. ^{1}H-NMR ($CDCl_3$): 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 $C_9H_7N_3S_2$: 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}. ^{1}H-NMR ($CDCl_3$): 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}. ^{1}H-NMR ($CDCl_3$): 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 $C_{10}H_9N_3OS_2$: 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}. ^{1}H-NMR ($CDCl_3$): 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 $C_9H_6ClN_3S_2$: C, 42.26; H, 2.36; N, 16.43. Found: C, 42.30; H, 2.51; N, 16.61.

REFERENCES

1. (a) M. Takahashi, S. Onda, and N. Matsumoto, *Synth. Commun*., 2006, **36**, 2087. (b) N. Matsumoto and M. Takahashi, *Tetrahedron Lett*., 2005, **46**, 5551. (c) N. Matsumoto and M. Takahashi, *Heterocycles*, 2003, **60**, 2677. (d) N. Matsumoto and M. Takahashi, *Tetrahedron,* 2002, **58**, 10073.
2. T. L. Gilchrist, C. J. Moody, and C. W. Rees, *J. Chem. Soc., Perkin Trans. 1,* 1975, 1964.
3. T. Fuchigami and K. Odo, *Chem. Lett*., 1974, 247.
4. H. Yoshida, T. Ogata, and S. Inokawa, *Bull. Chem. Soc. Jpn*., 1977, **50**, 3302.
5. M. Yokoyama and T. Inamoto, *Synthesis,* 1984, 797.
6. M. Sato, N. Fukada, M. Kurauchi, and T. Takeshima, *Synthesis,* 1981, 554.
7. R. Gompper and W. Hägele, *Chem. Ber*., 1966, **99**, 2885.
8. F. Merchan, J. Garin, and E. Melendez, *Synthesis*, 1982, 590.
9. K. Kamala, P. J. Rao, and K. K. Reddy, *Indian J. Chem. Sect. B*, 1983, **22B**, 1194 (*Chem. Abstr*., 1984, **101**, 110826k).
10. D. D. J. Cartwright, B. A. J. Clark, and H. McNab, *J. Chem. Soc., Perkin Trans. 1* , 2001, 424.