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Synthetic Applications of 3*H*-1,2,4-Dithiazoles: Structure and Reactivity Studies

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ABSTRACT: *Synthetic applications of 3H-1,2,4-dithiazoles have been studied extensively. The facile synthesis of hitherto unknown 3H-1,2,4-dithiazole S-oxides was realized by the mCPBA oxidation of 3H-1,2,4-dithiazoles. The structural information of the 1,2,4-dichalcogenazole ring system was revealed by the ORTEP analysis of 3-tert-butyl-5-4-chloro-phenyl-3H-1,2,4-dithiazole S-oxide. The reactivities of 3H-1,2,4-dithiazoles are also discussed.* © 2011 Wiley Periodicals, Inc. Heteroatom Chem 23:154–159, 2012; View this article online at wileyonlinelibrary.com. DOI 10.1002/hc.20764

INTRODUCTION

Many heterocyclic rings are found to be key components in biological systems. Heterocyclic scaffolds having nitrogen, sulfur, and oxygen atoms are playing a pivotal role in pharmaceutical chemistry and other fields due to their recognized biological profiles and unique multifunctional characteristics [1–4]. Reactive intermediates containing thiocarbonyl functionalities conjugated with nitrogen moiety have long been studied as versatile building blocks for the synthesis of useful heterocyclic compounds. A great deal of attention has been focused on the generation and synthetic application of α,β-unsaturated thione *S*-oxides and their thio variants (Chart 1) because of their heterocumulene-like structures and intriguing reactivity for the synthesis of various heterocycles. However, there have only been a few studies on the synthesis of thiocarbonyl *S*-sulfides (thiosulfines) possessing higher π-conjugation systems. In spite of their huge synthetic potentialities, this area remains unexplored. Therefore, the generation and synthetic applications of thiosulfoxides leading to heterocycles with multifarious purposes are being considered as a pragmatic area for current research [5–11]. Our strategy is to synthesize heterocycles having nitrogen and chalcogen moieties through generating highly reactive intermediates possessing chalcogen and nitrogen functionalities and their subsequent ring closure or trapping.

In this way, we have already developed a few methods for generating highly reactive building blocks (sulfine or thiosulfine) through the thermal cycloreversion of appropriate precursors [12–14]. In addition, a series of 3*H*-1,2,4-dichalcogenazoles **3**–**7** were synthesized by the reaction of 6*H*-1,3,5-oxachalcogenazines **1** or **2** with respective chalcogens, as shown in Scheme 1 [15].

As 1,2,4-dichalcogenzoles **3–7** are new compounds, detailed structural information on this new ring system is valuable for scientific purposes. In this regard, we tried to prepare a crystalline compound of this series with different of our methods, but all efforts were unsuccessful. We then turned our efforts to the preparation of any crystalline derivative of 1,2,4-dichalcogenzoles in this

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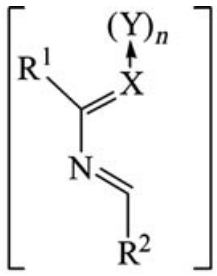


A: X = S, Y = 0, n = 0
B: X = S, Y = O, n = 1
C: X = S, Y = S, n = 1
D: X = Se, Y = 0, n = 0

CHART 1 Representative building blocks.

study, and finally, the crystalline compound of 3*H*-1,2,4-dithiazole-*S*-oxide **8b**. In addition to getting a structural overview of the 1,2,4-dichalcogenazole ring system, we were also interested in the synthetic applications of the 1,2,4-dichalcogenazole ring system. Herein, we report on the synthetic applications, characterization, and reactivity of the 3*H*-1,2,4-dithizoles ring system.

RESULTS AND DISCUSSION

Synthesis of 3H-1,2,4-Dithiazoles **3**

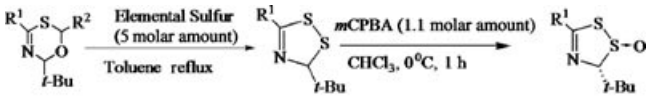
In the course of our studies on reactive building blocks for the synthesis of heterocyclic compounds, we developed a facile method for the synthesis of compounds **3** by the thermal reaction of 6*H*-1,3,5-oxathiazines **1** with elemental sulfur, as shown in Scheme 1 [15]. All of the compounds **3** were oily in nature. Characterization of 3*H*-1,2,4-dithiazoles **3** was carried out by measuring physical data, including MS, IR, ^{1}H NMR, ^{13}C NMR, and elemental analysis. The formation mechanism of **3** was suggested by the speculating [4 + 1]-type reaction between heretodiene **A**, generated through the thermal cycloreversion of **1**, and elemental sulfur [15].

Synthesis, Characterization, and Structure of 3H-1,2,4-Dithiazole S-oxides **8**

Since all of the 1,2,4-dichalcogenazoles **3–7** were oily in nature, obtaining clear structural information on the compounds was not possible from the X-ray analysis. Therefore, we attempted to synthesize a crystalline derivative of this series. In addition, it is a matter of great interest to find out the preferential oxidation site (sulfur atom) of heterocycles having a disulfide moiety. The oxidation of **3** having two sulfur atoms in the 1,2-positions by *m*CPBA (1.1 molar amount) at 0°C for 1 h afforded the corresponding sulfoxides **8** as a single epimer in nearly quantitative yields. Fortunately, the crystalline product **8b** was obtained with this approach. The spectral data, including MS, IR, ^{1}H NMR, and ^{13}C NMR, as well as the elemental analysis were fully consistent with the structures of 3-aryl-5-alkyl-3*H*-1,2,4-dithiazole *S*-oxides **8a–d**. The results for the synthesis of **3** and **8** are summarized in Table 1.

In the ^{1}H NMR spectrum, the peak ascribed to the methine proton of compound **3b** appeared at

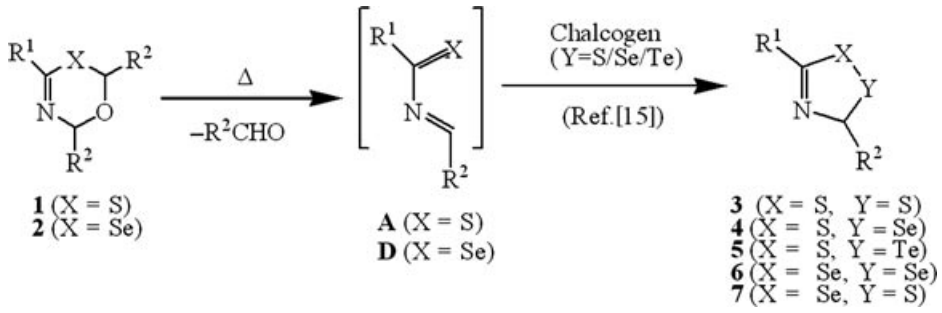
TABLE 1 Synthesis of 3H-1,2,4-Dithiazoles **3** and 3*H*-1,2,4-Dithiazole-*S*-oxides **8**



1 **3** **8**

Entry	Substrate R^1		Time (h)	Yield (%)[a] 3	Yield (%)[a] 8
1	C_6H_5	**1a**	15	88 (**3a**)	90 (**8a**)
2	*p*-ClC_6H_4	**1b**	25	91 (**3b**)	94 (**8b**)
3	*p*-FC_6H_4	**1c**	25	89 (**3c**)	92 (**8c**)
4	*p*-$CH_3OC_6H_4$	**1d**	15	98 (**3d**)	91 (**8d**)

[a]Isolated yields.



SCHEME 1 Synthesis of 1,2,4-dichalcozenazoles **3–7.**

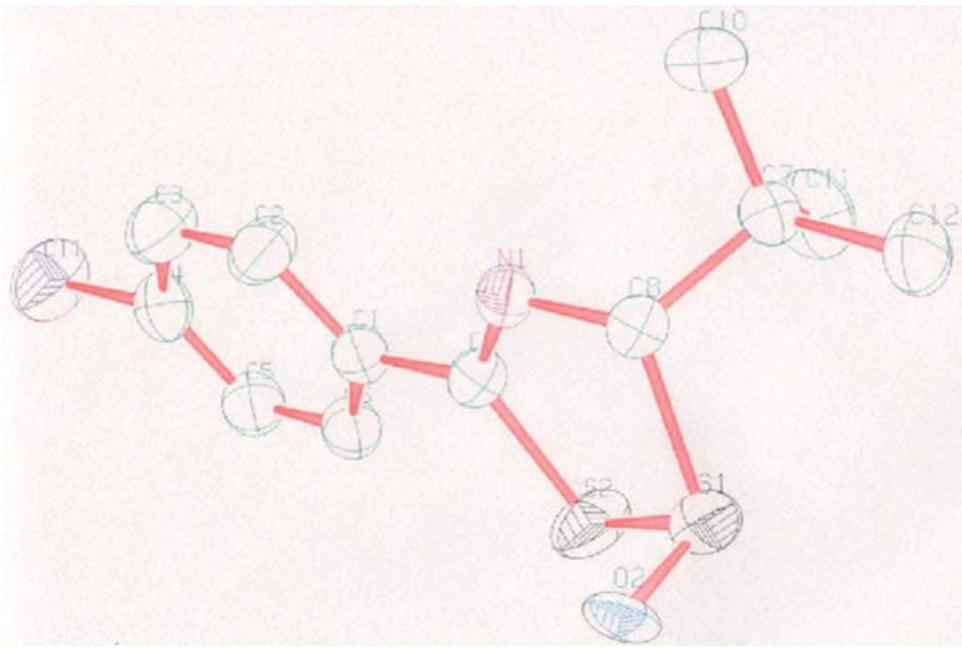


FIGURE 1 ORTEP drawing of **8b**. Selected bond lengths (Å), bond angles (.°), and torsion angles (.°): S1–O2 = 1.484(6); S1–S2 = 2.090(3); N1–C9 = 1.262(8); S2–S1-C8 = 91.5(2); S2–S1– O2=110.2(3); O2–S1–C8 = 104.4(3); C8–S1–S2–C9 = –16.9(2); O2–S1–S2–C9 = 89.1(2).

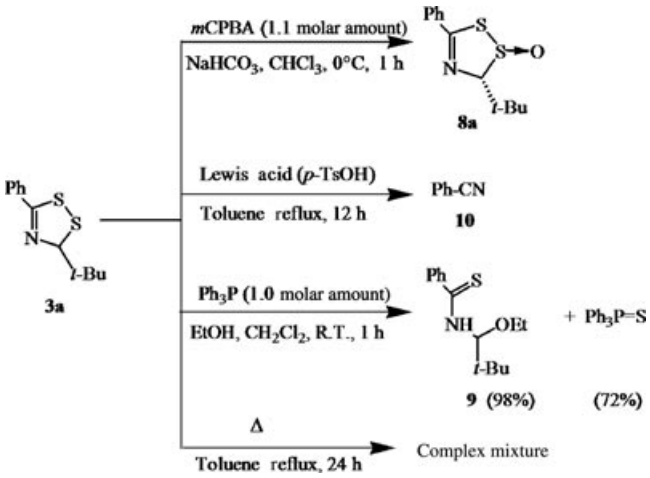
δ6.28, which shifted downfield by 0.32 ppm compared to that of the corresponding methine proton of **8b** (δ5.96). This might be due to the anisotropic effect of S=O groups. Therefore, the position of the newly introduced oxygen atom was assumed to be the S-2 atom of **8b** [16–18]. Finally, this speculation was unequivocally confirmed by the X-ray crystallographic analysis. The ORTEP drawing of **8b**, as shown in Fig. 1, demonstrates that the relative stereochemistry of the sulfinyl group at the S-2 atom is in a trans position to that of the nearby *t*-butyl group at the C-3 position. The delocalization of the electron pair on the sulfur atom of the 1-position might occur toward the C=N moiety, which possibly exposed the S-2 atom to oxidation. The final structural elucidation of compound **8b** by X-ray analysis would absolutely provide a reliable platform for exploring the core structure of the 1,2,4-dichalcogenazole ring system.

Colorless plates of **8b** suitable for X-ray investigation were obtained from hexane. Crystal data for **8b**: $C_{12}H_{14}ClNOS_2$, FW = 287.02, crystal size 0.30 × 0.20 × 0.10 mm^3, monoclinic, space group $P2_1/n$ (#14), a = 15.086(1), b = 6.0722(6), c = 15.711(1) Å, β = 110.651(4)°, V = 1346.8(2) Å^3, Z = 4, D_{calc} = 1.419 g/cm^3, μ = 5.76 cm^{-1}. From 25,338 reflections measured, 3362 were unique (R_{int} = 0.023). R = 0.070, R_w = 0.084, Mo Kα (λ = 0.71075 Å), T = 23°C. The structure was solved by using the direct method (SIR97).

Crystallographic data (excluding structure factors) have been sent to the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 219595. Copies of the data can be obtained, free of charge, via the Internet at http://www.ccdc.cam.ac.uk, or on application to the director at CCDC 219595, 12 Union Road, Cambridge CB2 1EZ, UK; tel.: (+44)1223-336-408; fax: (+44)1223-336-033; e- mail: deposit@ccdc.cam.ac.uk.

Synthetic Applications of 3H-1,2,4-Dithiazoles **3**

The salient feature of the reactivity of **3** is shown in Scheme 2. It was observed that compounds **3** were relatively stable for a long time. It was already mentioned in the preceding section that the *m*CPBA (1.1 molar amount) oxidation of **3** afforded **8** in nearly quantitative yields. When a toluene solution of **3a** was heated with *p*-toluenesulfonic acid (1.1 molar amount) at the refluxing temperature, **10** was produced in a 43% yield, along with some unidentified compounds. The reaction of **3a** with Ph_3P in the presence of EtOH at room temperature gave **9** (1,4-adduct of heterodiene **A**) in a 98% yield, along with Ph_3P=S in a 72% yield. On the other hand, when this



SCHEME 2 Reactivity of 3*H*-1,2,4-dithiazoles **3**.

reaction was conducted in the absence of EtOH, a complex mixture was obtained. It is speculated that a thiophilic attack of Ph_3P occurred at the sulfur atom (in 2-position) of **3a**, which subsequently extruded the sulfur atom from the ring, resulting in 1,3-thiaza-1,3-butadiene **A** at room temperature. This is a new approach for the generation of heterodiene **A** at a low temperature by using **3** as the precursor.

CONCLUSION

The synthetic applications of the 3*H*-1,2,4-dithiazole ring system have been investigated. A facile synthesis of novel 3*H*-1,2,4-dithiazole*S*-oxides **8** was realized by the simple *m*CPBA oxidation of 3*H*-1,2,4-dithiazoles **3**. The structural feature of 3*H*-1,2,4-dithiazole-*S*-oxide **8b** was uncovered by an X-ray analysis. The reactivity of 3*H*-1,2,4-dithiazoles **3** was studied. Further studies for the extensive utilization of the 1,2,4-dichalcogenazole ring system are in progress.

EXPERIMENTAL

General

Melting points were measured in open capillary tubes with a Buchi 535 micromelting point apparatus and are uncorrected. ^{1}H NMR spectra were determined at 400 MHz (Bruker AC-400P spectrometer), and ^{13}C NMR spectra were determined at 100 MHz (Bruker AC-400P spectrometer). Chemical shifts are expressed in parts per million (δ units) downfield from tetramethylsilane which was used as an internal reference. Mass spectra were recorded on a Hitachi M-2000 mass spectrometer with electronimpact ionization at 20 or 70 eV using a direct inlet system. IR spectra were recorded for thin film (neat) or KBr disks on a Jasco FT/IR-7300 spectrometer. Elemental analyses were performed using a Yanagimoto CHN recorder MT-5. Column chromatography was performed using silica gel (Merck, cat. no. 7734) without pretreatment. All substrates and reagents were commercially available in a reagent grade and were used without further pretreatment.

*General Procedure for the Synthesis of 3H-1,2,4-Dithiazoles (***3***)*

A toluene solution of **1a–d** (1.0 mmol) was treated with a 5 molar amount of elemental sulfur at a refluxing temperature for 12 h. The solvent was evaporated in vacuo, sulfur was removed from the resulting crude product by filtration, and the filtrate was subjected to chromatographic separation on Al_2O_3 to afford 3*H*-1,2,4-dithiazoles **3** in moderate to excellent yields.

3-tert-Butyl-5-phenyl-3H-[1,2,4]dithiazole, **3a** *[14].* Pale yellow oil; MS *m/z* (%) 237 (M^+; 18), 205 (M^+– S, 1), 180 (M^+– C_4H_9; bp); IR (neat): 2961, 1633, 1448, 1363, 1046, 928, 689, 602 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ1.13 (9H, s), 6.31 (1H, s), 7.40–7.48 (3H, m), 7.83–7.85 (2H, m); ^{13}C NMR ($CDCl_3$): δ26.7 (q), 38.9 (s), 104.1 (d), 128.7 (d), 128.9 (d), 131.7 (d), 132.1 (s), 165.1 (s); Found: C, 60.91; H, 6.56; N, 5.89%. Calcd. for $C_{12}H_{15}NS_2$: C, 60.71; H, 6.37; N, 5.90%.

*3-tert-Butyl-5-(4-chloro-phenyl)-3H-[1,2,4]dithiazole,***3b** *[14]* . Pale yellow oil; MS *m/z* (%) 271 (M^+; 15), 239 (M^+– S, 2), 214 (M^+– C_4H_9; bp); IR (neat): 2961, 1623, 1488, 1363, 1253, 1093, 927, 832, 590 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ1.10 (9H, s), 6.29 (1H, s), 7.39 (2H, d, J = 8.4 Hz), 7.77 (2H, d, J = 8.5 Hz); ^{13}C NMR ($CDCl_3$): δ26.7 (q) 38.9 (s), 104.0 (d), 128.4 (s), 128.5 (s), 128.9 (d), 130.2 (d), 69.6 (s); Found: C, 53.28; H, 5.33; N, 4.62%. Calcd. for $C_{12}H_{14}ClNS_2$: C, 53.02; H, 5.19; N, 5.15%.

3-tert-Butyl-5-(4-fluoro-phenyl)-3H-[1,2,4]dithiazole, **3c** *[14]* . Pale yellow oil; MS *m/z* (%) 255 (M^+; 18), (M^+– S, 223), 198 (M^+– C_4H_9; bp); IR (neat): 2962, 1629, 1507, 1236, 1046, 929, 840, 601 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ1.10 (9H, s), 6.28 (1H, s), 7.10 (2H, t, J = 8.5 Hz), 7.84 (2H, dd = 5.3, 5.4 Hz); ^{13}C NMR ($CDCl_3$): δ26.6 (q), 38.8 (s), 104.0 (d), 115.7 (d), 115.9 (d), 131.0 (d), 131.1 (d), 163.8 (s), 164.8 (d, J = 251.4 Hz); Found: C, 56.89; H, 5.48; N, 5.17%. Calcd. for $C_{12}H_{14}FNS_2$: C, 56.44; H, 5.53; N, 5.48%.

3-tert-Butyl-5-(4-methoxy-phenyl)-3H-[1,2,4]dithiazole, **3d** *[14]* . Pale yellow oil; MS *m/z* (%) 267 (M^+; 11), 235(M^+– S, 3), 210 (M^+– C_4H_9; bp); IR (neat): 2961, 1606, 1509, 1257, 1173, 926, 835, 600 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ1.10 (9H, s), 3.84 (3H, s), 6.26 (1H, s), 6.91 (2H, d, J = 8.8 Hz), 7.80 (2H, d, J = 8.8 Hz); ^{13}C NMR ($CDCl_3$): δ26.7 (q), 38.8 (s), 55.4 (q), 104.0 (d), 113.9 (d), 124.8 (s), 130.7 (d), 139.1 (s), 164.3 (s); Found: C, 58.67; H, 6.23; N, 4.96%. Calcd. for $C_{13}H_{17}NOS_2$: C, 58.39; H, 6.41; N, 5.24%.

Synthesis of 3H-1,2,4-Dithiazoles S-oxides **8** *by mCPBA Oxidation of 3H-1,2,4 Dithiazoles* **3**

A chloroform solution (20 mL) of 3*H*-1,2,4-dithiazoles (**3**, 1.0 mmol) was treated with *m*CPBA (1.1 molar amount) at 0°C for 1 h in the presence of $NaHCO_3$(2 molar amount). The reaction mixture was quenched with aqueous Na_2SO_3solution and was extracted with chloroform. The mixture was then subjected to the usual workup. The solvent was evaporated in vacuo, and the crude product was subjected to chromatographic separation on silica gel. The products 3*H*-1,2,4-dithiazole *S*-oxides **8** were obtained in a high yield.

3-tert-Butyl-5-phenyl-3H-[1,2,4]dithiazole S-oxide, **8a**. Colorless oil; MS *m/z* (%) 237 (M^+– O; 2), 221 (M^+– S, 1), 158 (bp); IR (neat): 2963, 1634, 1474, 1148, 1084, 1056, 689 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ1.15 (9H, s), 5.98 (1H, s), 7.46–7.55 (3H, m), 7.92–7.95 (2H, m); ^{13}C NMR ($CDCl_3$): δ27.5 (q), 37.4 (s), 128.9 (d), 129.5 (d), 12987 (d), 131.0 (s), 132.3 (d), 160.6 (s); Calcd. for $C_{12}H_{15}NOS_2$: C, 56.88; H, 5.97; N, 5.53%; Found: C, 57.02; H, 5.98; N, 5.39%.

3-tert-Butyl-5-(4-chloro-phenyl)-3H-[1,2,4]dithiazole S-oxide, **8b**. Colorless needles, mp 88–89°C; MS *m/z* (%) 271 (M^+– O; 3), 207 (M^+– S_2O, 12), 192 (bp); IR (KBr): 2962, 1624, 1488, 1399, 1083, 1056, 920, 618 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ1.16 (9H, s), 5.96 (1H, s), 7.45 (2H, d, J = 8.6 Hz), 7.87 (2H, d, J = 8.6 Hz); ^{13}C NMR ($CDCl_3$): δg g27.5 (q), 37.5 (s), 129.2 (s), 129.3 (d), 129.5 (d), 130.4 (s), 131.0 (d), 159.5 (s); Calcd. for $C_{12}H_{14}ClNOS_2$: C, 50.07; H, 4.90; N, 4.87%; Found: C, 50.23; H, 4.91; N, 4.74%.

3-tert-Butyl-5-(4-fluoro-phenyl)-3H-[1,2,4]dithiazole S-oxide, **8c**. Colorless oil; ^1H NMR (400 MHz, $CDCl_3$): δ1.15 (9H, s), 5.96 (1H, s), 7.16 (2H, t, J = 8.5 Hz), 7.95 (2H, dd, J = 5.3, 5.2 Hz); ^{13}C NMR ($CDCl_3$): δ27.5 (q), 37.4 (s), 116.1 (d, J = 23.1 Hz), 128.0 (d), 129.4 (d), 131.8 (s), 131.9 (d), 159.2 (s), 165.0 (d, J = 251.8 Hz); Calcd. for $C_{12}H_{14}FNOS_2$: C, 53.11; H, 5.20; N, 5.16%; Found: C, 53.28; H, 5.22; N, 4.95%.

3-tert-Butyl-5-(4-methoxy-phenyl)-3H-[1,2,4]dithiazole S-oxide, **8d**. Colorless oil; MS *m/z* (%) 267 (M^+ – O; 7), 203 (M^+– S_2O, 13), 188 (bp); IR (neat): 2962, 1604, 1509, 1464, 1079, 1057, 603 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ1.14 (9H, s), 3.87 (3H, s), 5.96 (1H, s), 6.96 (2H, d, J = 8.8 Hz), 7.88 (2H, d, J = 8.8 Hz); ^{13}C NMR ($CDCl_3$): δ 27.5 (q), 37.4 (s), 55.5 (q), 114.3 (d), 124.4 (s), 129.7 (d), 131.6 (d), 136.4 (s), 162.8 (s); Calcd. for $C_{13}H_{17}NO_2S_2$: C, 55.09; H, 6.05; N, 4.94%; Found: C, 55.15; H, 6.02; N, 4.36%.

N-(1-Ethoxy-2,2-dimethyl-propyl)-thiobenzamide, **9**. Pale yellow oil, (lit. [8]); ^1H NMR ($CDCl_3$): δ1.04 (9H, s), 1.19 (3H, t, J= 5.5 Hz), 3.64 (2H, dq, J = 5.3 Hz), 5.81 (1H, d, J = 9.5 Hz), 7.39 (3H, m), 7.74 (2H, d, J = 7.1 Hz).

Benzonitrile, **10**. Colorless oil; MS *m/z* (%) 103 (M^+, bp), 104.05 (M^+, 7.9%), 76 (M^+– CN, 28); IR (neat): 2962, 1604, 1509, 1464, 1079, 1057, 603 cm-^{1}; ^1H NMR (400 MHz, $CDCl_3$): δ7.34(2H, d, J = 8.1 Hz), 7.38 (3H, m); ^{13}C NMR ($CDCl_3$): δ 112.5 (s), 118.9 (s), 129.3 (d), 132.3 (d), 132.9 (d); Calcd. for C_7H_5N: C, 81.53; H, 4.89; N, 13.58%; Found: C, 81.65; H, 4.91; N, 13.47%.

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REFERENCES

[1] Li, J. -J.; Johnson, D. S.; Sliskovic, D. R.; Roth, B. D. Contemporary Drug Synthesis; Wiley: Hoboken, NJ, 2004.
[2] Kolos, N. N.; Tishchenko, A. A.; Orlov, V. D.; Berezkina, T. V.; Shishkina, S. V.; Shishkin, O. V. Chem Heterocycl Compd 2001, 37, 1289.
[3] Sato, R. Pure Appl Chem 1999, 489–494.
[4] Gupta, A.; Mishra, P.; Kashaw, S. K.; Jatav, V. Indian J Pharm Sci 2008, 70, 535–538.
[5] Tanaka, S.; Suguhara, Y.; Sakamoto, A.; Ishii, A.; Nakayama, J. J Am Chem Soc 2003, 125, 9024–9025.
[6] Huisgen, R.; Rapp, J. J Am Chem Soc 1987, 109, 902–903.
[7] Kuipers, J. A. M.; Lammerink, B. H. M.; Still, I. W. J.; Zwanenburg, B. Synthesis 1981, 295–297.

[8] Shimada, K.; Aikawa, K.; Fujita, T; Sato, M; Goto, K; Aoyagi, S.; Takikawa, Y.; Kabuto, C. Bull Chem Soc Jpn 2001, 74, 511–525.
[9] Kutney, G. W.; Turnbull, K. Chem Rev 1982, 82, 333–357.
[10] Okuma, K.; Shigetomi, T.; Nibu, Y.; Shioji, K.; Yoshida, M., Yokomori, Y. J Am Chem Soc 2004, 126, 9508–9509.
[11] Romański, J.; Reisenauer, H. P.; Petzold, H.; Weigand, W.; Schreiner, P. R.; Mloston, G. Eur J Org Chem 2008, 2998–3003.
[12] Shimada, K.; Rafiqul, I. M.; Sato, M.; Aoyagi, S.; Takikawa, Y. Tetrahedron Lett 2003, 44, 2517–2519.
[13] Rafiqul, I. M.; Shimada, K.; Aoyagi, S.; Takikawa, Y.; Kabuto, C., Heteroatom Chem 2004, 15, 175–186.
[14] Rafiqul, I. M.; Shimada, K.; Aoyagi, S.; Fujisawa, Y.; Takikawa, Y. Heteroatom Chem 2004, 15, 208–215.
[15] Rafiqul, I. M.; Shimada, K.; Aoyagi, S.; Fujisawa, Y.; Takikawa, Y. Tetrahedron Lett 2004, 45, 6187–6190.
[16] Buck, K. W.; Hamor, T. A.; Watkin, D. J. J Chem Soc, Chem Commun 1966, 759.
[17] Foster, A. B.; Inch, T. D.; Qadir, M. H.; Webber, J. M. J Chem Soc, Chem Commun 1968, 1086.
[18] Nakayama, J.; Furuya, T.; Ishii, A.; Sakamoto, A.; Otani, T.; Sugihara, Y. Bull Chem Soc Jpn 2003, 76, 619–625.