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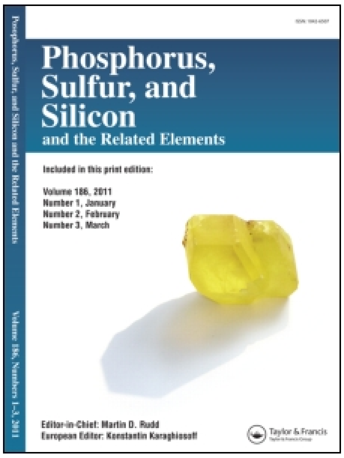

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Preparation, Thermolysis, and Photolysis of Some New Thiophosphoramidates Derived from 3-Methyl-2-Benzothiazolinone Hydrazone

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Online publication date: 23 March 2010

To cite this Article Yosef, Hisham Abdallah A.(2010) 'Preparation, Thermolysis, and Photolysis of Some New Thiophosphoramidates Derived from 3-Methyl-2-Benzothiazolinone Hydrazone', Phosphorus, Sulfur, and Silicon and the Related Elements, 185: 4, 890 — 897

To link to this Article: DOI: 10.1080/10426500903023087

URL: http://dx.doi.org/10.1080/10426500903023087

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Phosphorus, Sulfur, and Silicon, 185:890–897, 2010
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ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500903023087

PREPARATION, THERMOLYSIS, AND PHOTOLYSIS OF SOME NEW THIOPHOSPHORAMIDATES DERIVED FROM 3-METHYL-2-BENZOTHIAZOLINONE HYDRAZONE

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3-Methyl-2-benzothiazolinone hydrazone (1) reacts with dialkyl phosphorothiochloridates 2a,b in the presence of a base, to give the respective dialkylthiophosphorylated hydrazones 3a,b. Upon thermolysis, compound 3b yields bi(3-methylbenzothiazole-2-iminyl) (4). Exposure of 3b to sunlight in methanol results in the formation of 3-methyl-2-benzothiazolinone (5). When the same experiment was carried on the starting hydrazone 1, bis(3-methylbenzothiazole-2-iminyl)diazine (6) was formed. Elemental analyses and spectroscopic details are presented for the new compounds.

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Keywords 3-Methyl-2-benzothiazolinone hydrazone; photolysis; thermolysis; thiophosphorylation; X-ray crystallography

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INTRODUCTION

Organophosphorus esters and thioesters are widely used in industry,[1] organic synthesis,[2] and agriculture.[3–5] Besides, thiophosphoramidates are of particular interest by virtue of being considered as eco-friendly agrochemicals, and their potential biological activities have been reported in several occasions.[6] They also have wide applications in peptide synthesis[7] and reactions with carbonyl compounds to prepare a variety of imines and heteroallenes.[8] In addition, thiazole derivatives are known to evoke diverse pharmacological potentialities including antibacterial,[9] anti-inflammatory,[10] and antiviral[11–13] activities. It thus appeared to be of interest to design the present study aimed at preparing new thiophosphoramidates through thiophosphorylation of 3-methyl-2-benzothiazolinone hydrazone (**1**). Structures of the new products are confirmed by IR[14] and ^{1}H NMR spectroscopy[15] as well as mass spectrometry.[16]

RESULTS AND DISSCUSION

It has now been found that phosphorylation of compound **1** with dialkyl phosphorothiochloridates **2a**,**b** proceeds in acetonitrile at room temperature in the

Received 8 February 2009; accepted 6 May 2009.
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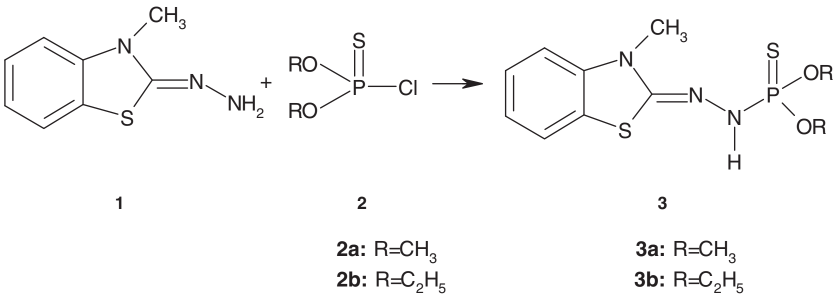

Scheme 1 Synthesis of thiophosphoramidates **3a**,**b**.

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presence of an acid-binding agent to give the respective thiophosphoramidates **3a**,**b** (Scheme 1).

Compatible elementary and molecular weight determination (MS) were gained for both products. For example, the IR spectrum of **3b** (KBr, cm^{-1}) showed strong absorption bands at 3174 (N—H), 2920, 2890 (C—H, aliphatic), 1600 (C=N), 1580 (C=C) and 1105 ($P-O-C_2H_5$). Its ^1H NMR spectrum (DMSO-d_6, δ ppm) showed signals at 1.24 (t, $^3J_{HH} = 6.9$ Hz, 6H, $O-C-CH_3$), 3.38 (s, 3H, $N-CH_3$), 4.07 (q, $^3J_{HH} = 6.9$ Hz, 4H, $O-CH_2-C$), 7.03–7.50 (m, 4H, aromatics) and at 8.02 (1H, N—*H*, exchangeable with D_2O). The mass spectrum of **3b** (Scheme S1, available online in the Supplemental Materials) showed the molecular ion peak at *m/z* 331 (100%). Cleavage of M^+ at axis **x** affords cation **a** at m/z 178 (58.5%), which can undergo molecular rearrangement followed by ejection of N_2 molecule to afford cation **c** at *m/z* 150 (24%). Loss of a hydrogen radical from ion **c** produces the prominent radical cation **d** at *m/z* 149 (91%). The molecular ion peak can also undergo loss of an ethoxyl radical to yield cation **e** at *m/z* 286 (1.7%). The prominent ion peak at *m/z* 109 (ion **g**, 42.3%) can originate via cleavage of the thiazole ring under electron impact followed by abstraction of a hydrogen radical by the resulting episulphide radical cation **f** at *m/z* 108 (12.4%).

Moreover, the structure **3b** has been unambiguously confirmed by a single crystal X-ray crystallographic analysis. An ORTEP projection of **3b** is shown in Figure 1.

Since the stability of phosphorus compounds and their activity are liable to change due to many environmental factors,[17–20] a study on the effects of heat[17,18] and light[19–21] on thiophosphoramidate **3b** is now undertaken. Thus, compound **3b** was subjected to thermolysis in a cold finger sublimator at about 220°C (bath temperature) under reduced pressure. The substance that remained in the tube was collected and crystallized from toluene to give a yellow compound formulated as bi(3-methyllbenzothiazole-2-iminyl) (**4**) (Scheme S2, Supplementary Materials) for the following reasons:

1. Elemental and molecular weight determination (MS) (M^+, *m/z* 326, 100%) for compound **4** corresponded to a molecular formula of $C_{16}H_{14}N_4S_2$.
2. Its IR spectrum (KBr, cm^{-1}) lacked the absorption due to N—H and $P-O-C_2H_5$ groupings expected around 3200 and 1100 cm^{-1}, respectively. On the other hand, strong bands were recorded in the spectrum of **4** at 3060 (C—H, aromatic), 2920 (CH_3), 1610 (C=N), and 1570 (C=C, aromatic).
3. The ^1H NMR spectrum of **4** (DMSO-d_6) showed no signals due to the ethoxyl groups.

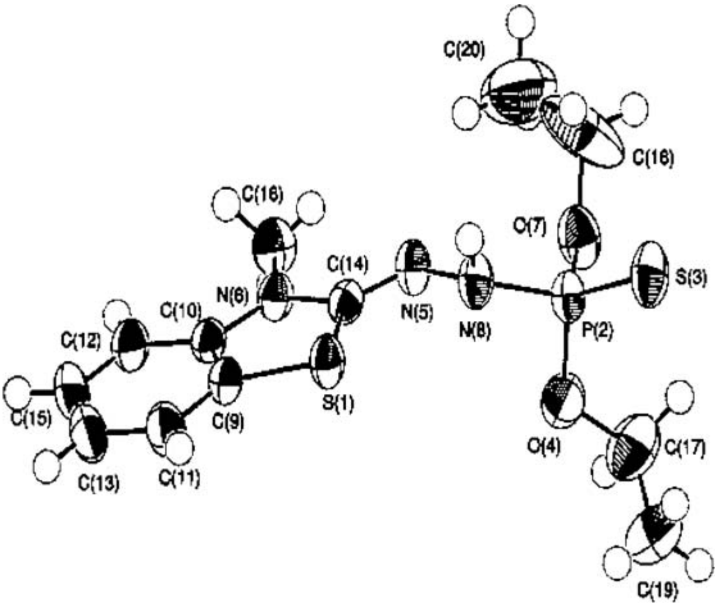

Figure 1 ORTEP diagram of compound **3b**.

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It showed also no signals exchangeable with D_2O (N*H*). However, the singlet that appeared at $\delta = 3.64$ ppm is attributed to the two methyl groups. X-ray crystallographic analysis confirmed that compound **4** has the less sterically crowded antiperiplanar conformation (Figure 2).

Exposure of **3b** to sunlight in methanol resulted in its total conversion after 60 days (TLC) to a colorless crystalline substance identified as 3-methyl-2-benzothiazolinone (**5**) (Scheme S3, Supplemental Materials), for the following reasons:

1. Compatible elemental and molecular weight determination (MS) (M^+, *m/z* 165, 100%) corresponded to a molecular formula of C_8H_7NOS.
2. Its IR spectrum showed a strong band at 1688 cm^{-1} attributable to the carbonyl group absorption of the thiazolone ring.

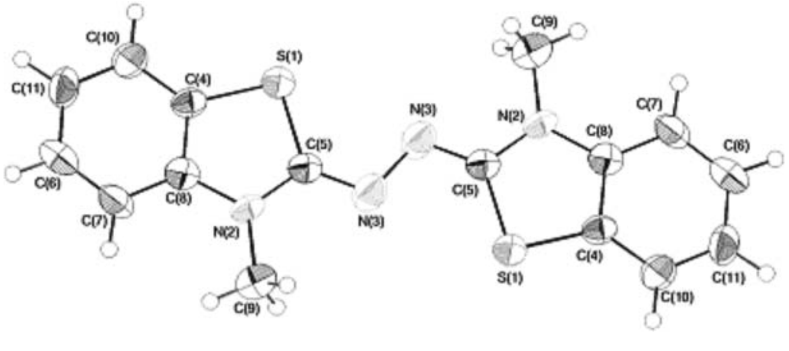

Figure 2 ORTEP diagram of compound **4**.

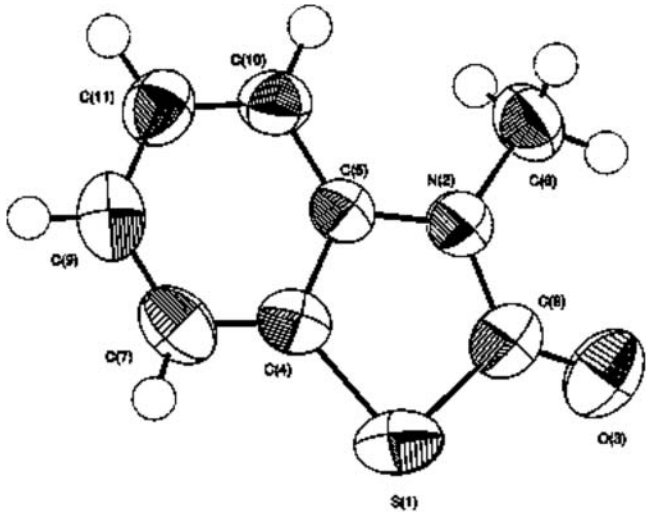

Figure 3 ORTEP diagram of compound **5**.

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3. The ^{1}H NMR spectrum of **5** ($CDCl_3$) showed no absorption bands for protons of the ethoxyl groups. It showed also no signals for D_2O-exchangable protons (N*H*).

The structure of compound **5** was confirmed by single crystal X-ray analysis (Figure 3).

A comparative study on the starting hydrazone **1** was also undertaken. Thus, when compound **1** was subjected to sunlight irradiation in methanol, about 70% conversion of **1** was completed (60 days) to give a dehydrodimerization product formulated as bis(3-methylbenzothiazole-2-iminyl)diazine (**6**) (Scheme S4, Supplemental Materials).

Structure **6** has been assigned for the following reasons:

1. Satisfactory elemental analyses and molecular weight determination (M^+, *m/z* 354, 24%) corresponded to a molecular formula of $C_{16}H_{14}N_6S_2$. Ejection of N_2 molecule from the molecular ion peak gave a radical cation at *m/z* 326 (8%).
2. Its IR spectrum showed no absorption for N-H bands.
3. The ^{1}H NMR spectrum (DMSO-d_6) showed two singlets at $\delta = 3.48$ and 3.74 ppm for the methyl groups. The multiplet that appeared in the region 7.00–7.87 ppm is attributed to the aromatic protons. The spectrum showed no signals exchangeable with D_2O (N*H*).
4. An analysis of the X-ray crystallographic data showed that two independent molecules of compound **6** are present in the same asymmetric unit cell and both of them have the *trans*-configuration. However, the two molecules differ in torsion angle between the planes of the two benzothiazole rings. This may explain the appearance of two singlets due to the methyl groups in ^{1}H NMR spectrum of compound **6** (Figure 4).

CONCLUSION

The present study describes a simple and direct method for the preparation of new organophosphorus compounds **3a**,**b** derived from benzothiazole heterocyles that may attract interest, particularly as eco-friendly pesticides. The –N-N- linkage in **3b** is the most

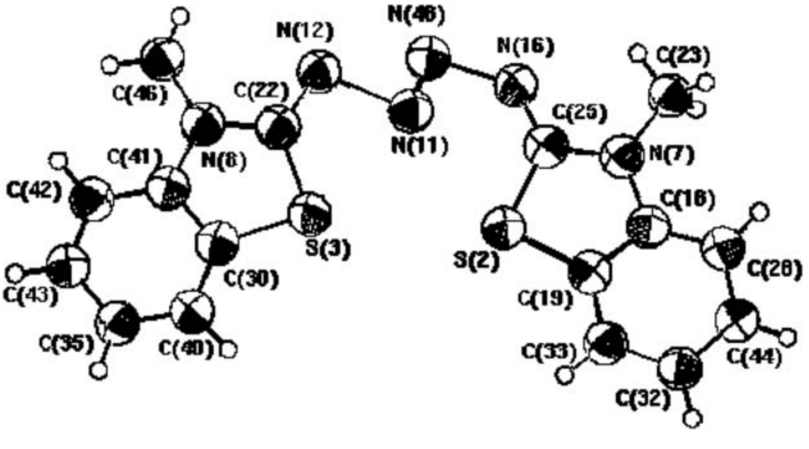

Figure 4 ORTEP diagram of compound **6**.

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vulnerable site of attack due to thermolysis leading to a dimeric product of type **4**. Photolysis of thiophosphoramidate **3b**, however, may proceed via cleavage of the exocyclic —C=N double bond by singlet oxygen, which has been afforded from the compound itself (act as a sensitizer) to yield the benzothiazolinone **5**. This process requires a long exposure period (60 days), which denotes the relative stability of **3b** to solar UV-irradiation. Under the same conditions, on the other hand, the photolysis of the starting hydrazone **1** affects the amino group leading to dehydrodimerization and formation of compound **6**.

EXPERIMENTAL

Reactions with phosphorothiochloridates were carried under an atmosphere of dry argon. Solvents were purified and dried according to the usual procedures. 3-Methyl-2-benzothiazolinone hydrazone was prepared according to a given procedure.[22] Phosphorothiochloridates **2a**,**b** are commercially available (Aldrich). The photo-experiments were carried out in Schlenk[23] tubes of Pyrex glass. The tubes were sealed while a stream of dry argon gas was passing through. Column chromatography was performed using silica gel, grain size 0.063–0.2 mm (Merck). Melting points were recorded on an Electrothermal melting point apparatus and were uncorrected. The infrared spectra were obtained from KBr-disks using a JASCO FT/IR-300E Fourier Transform Infrared Spectrophotometer and reported in cm^{-1}. ^1H NMR spectra were recorded on JOEL 500 AS equipment (at 500 MHz). Proton chemical shifts (δ) are reported in ppm downfield from TMS. Mass spectra were recorded on a Finnigan SSQ 7000 Spectrometer at 70 eV.

X-Ray Diffraction

Intensity data collection was performed with a Kappa-CCD Enraf Nonius FR 590 Single Crystal Diffractometer. The structures were solved by direct methods using the *SIR*92 program[24] and refined using ma*X*us.[25] The molecular graphics were made with ORTEP.[26] Crystallographic data (CIF) for the structures reported in this article have been deposited in the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication No. 711837–711840. Copies of the data can be obtained, free of charge, upon application to the

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Table I Crystal structure and data refinement parameters used for the intenisty data collection strategy and final results of the structure determination*

Compound	**3b**	**5**	**6**
Empirical formula	$C_{12}H_{18}N_3O_2PS_2$	C_8H_7NOS	$C_{32}H_{28}N_{12}S_4$**
Formula weight	331.397	165.214	708.0916**
Crystal system/space group	Triclinic/P1	Orthorombic/Pbca	Monoclinic/$P2_1/c$
a / Å	9.0168(2)	10.8218(3)	15.8725(3)
b / Å	9.7413(2)	8.4278(3)	6.7582(2)
c / Å	10.4070(3)	16.957(9)	31.8224(9)
α / °	103.8146(11)	90.00	90.00
β / °	107.1879(12)	90.00	100.5112
γ / °	102.3738(13)	90.00	90.00
V / $Å^3$	807.05(3)	1546.59(12)	3356.3(2)
Z	2	8	4
D_{calc} (Mg/m^3)	1.364	1.419	1.403
μ (mm^{-1})	0.43	0.35	0.33
Color/shape	Colorless/prismatic	Colorless/prismatic	Brown/cube
Theta range for collection	2.91–27.485	2.91–25.35	2.91–21.036
Reflections collected	5126	2819	6240
Independent reflections	3866	1556	3882
Data/restraints/parameters	2760 / 0 / 181	927 / 0 / 115	1784 / 0 / 433
Goodness of fit on F^2	0.865	1.227	2.516
Final R indices [$I > 3\sigma(I)$]	0.041	0.034	0.053
R indices (all data)	0.057	0.066	0.134
Largest difference peak/hole	0.39 / –0.30	0.24 / –0.22	0.48 / –0.45

*Temperature: 298 K, wavelength: MoK_α (0.71073 Å).

**Two independent molecules are present in the same asymmetric unit cell, therefore the value is doubled.

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The X-Ray crystallographic data are represented in Table I. We have utilized X-ray crystallography in conjunction with other techniques to confirm the structure described.

Reaction of Hydrazone 1 with Dialkyl Phosphorothiochloridates 2a,b

To a stirred solution of the hydrazone **1** (0.01 mol) in dry acetonitrile (100 mL), dry K_2CO_3 (5 g) was added, and stirring was continued at room temperature for 1 h. The appropriate phosphorothiochloridate **2a** or **b** was added, and the mixture was stirred for a further 48 h at room temp. After removal of the inorganic materials by filtration, the volatile materials were removed from the filtrate under reduced pressure. The residual material was collected and recrystallized from the appropriate solvent to give compounds **3a**,**b**.

N-Dimethoxythiophosphoryl-3-methyl-2-benzothiazolinone Hydrazone (3a). Colorless crystals from cyclohexane; Yield: 73%. mp 108–110°C. IR: 3187 (N—H), 3040 (C—H, aromatic), 2950, 2840 (C—H, aliphatic), 1595 (C=N), 1571 (C=C, aromat.), 1074 (P—O—CH_3), 930 (P—N), 648 (P=S). ^1H NMR ($CDCl_3$): 3.47 (s, 3H, N—CH_3), 4.83 (d, $^3J_{HP} = 14$ Hz, 6H, O—CH_3), 5.60 (1H, N—H exchangeable with D_2O), 6.93–7.36 (m, 4H, aromatics). MS: m/z% = 303 [M^+, 100]. Anal. Calcd. (%) for $C_{10}H_{14}N_3O_2PS_2$ (303.33): C, 39.60; H, 4.65; N, 13.85; P, 10.21; S, 21.14; Found (%): C, 39.72; H, 4.51; N, 13.71; P, 10.1; S, 20.93.

N-Diethoxythiophosphoryl-3-methyl-2-benzothiazolinone Hydrazone (3b). Colorless crystals from petroleum ether b.r. 80–100°C; Yield: 85%; mp 122–123°C; IR: 3174 (N—H), 2972 (C—H, aromatic), 2920, 2890 (C—H, aliphatic), 1600 (C=N), 1580 (C=C, aromatic), 1105 (P—O—C_2H_5), 930 (P—N), 646 (P=S); ^{1}H NMR (DMSO-d_6): 1.24 (t, $^3J_{HH} = 6.9$ Hz, 6H, O—C—CH_3), 3.38 (s, 3H, N-CH_3), 4.07 (q, $^3J_{HH} = 6.9$ Hz, 4H, O—CH_2—C—), 7.03—7.50 (m, 4H, aromatics), 8.02 (1H, N—*H* exchangeable with D_2O). MS: m/z% = 331 [M^+, 100]. Anal. Calcd. (%) for $C_{12}H_{18}N_3O_2PS_2$ (331.39): C, 43.49; H, 5.47; N,12.68; P,9.35; S,19.35. Found (%): C, 43.56; H, 5.33; N,12.89; P, 9.66; S,19.1.

Thermolysis of 3b

Compound **3b** (0.5 g) was heated in a cold finger sublimator at 220°C (bath temperature) under reduced pressure (0.5 mm/Hg) for about 30 min. The residue in the sublimator was collected and recrystallized to give bi(3-methyllbenzothiazole-2-iminyl) (**4**). Yellow crystals from toluene; Yield: 94%; mp 266°C. IR: 3060 (C—H, aromatic), 2920 (C—H, aliphatic), 1610 (C=N), 1570 (C=C, aromatic). ^{1}H NMR (DMSO-d_6): 3.46 (s, 6H, N—CH_3), 7.00–7.52 (m, 8H, aromatics). MS: m/z%: 326 [M^+, 100]. Anal. Calcd (%) for $C_{16}H_{14}N_4S_2$ (326.43): C, 58.87; H, 4.32; N, 17.16; S, 19.64. Found (%): C, 59.14; H, 4.13; N, 16.91; S, 19.84.

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Photochemical Action of Sunlight on Compound 3b in Methanol

A solution of **3b** (0.006 mol, 2 g) in dry methanol (200 mL) was exposed to sunlight for 60 days (September–October) until **3b** disappeared (TLC). The volatile materials were removed under reduced pressure, and the residue was chromatographed on silica gel to give 3-methyl-2-benzothiazolinone (**5**) after elution with petroleum ether b. r. 60–80°C/acetone (80:20).

3-Methyl-2-benzothiazolinone (5). Colorless crystals, yield 87%, mp 72°C (Lit.[27] 72°C). IR: 3040 (C—H, aromatic), 2930 (C—H, aliphatic), 1688 (C=O). ^{1}H NMR ($CDCl_3$): 3.45 (s, 3H, N—CH_3), 7.03–7.43 (m, 4H, aromatics). MS: m/z%: 165 [M^+, 100].

Photochemical Action of Sunlight on the Hydrazone 1 in Methanol

A solution of **1** (0.011 mol, 2 g) in dry methanol (200 mL) was exposed to sunlight for 60 days. At the end of the experiment, the volatile materials were removed under reduced pressure, and the residue was chromatographed on silica gel to give bis(3-methyl benzo- thiazole-2-iminyl)diazine (**6**) after elution with petroleum ether 60–80°C/acetone (50:50). About 30% (600 mg) of unchanged hydrazone **1** was also recovered after elution with petroleum ether 60–80°C/acetone (90:10), (mp, mixed mp, MS, and comparative IR spectra).

Bis(3-methylbenzothiazole-2-iminyl)diazine (6). Brown crystals from toluene, yield 67%, mp 194°C, IR: 3386, 3173 (N—H), 3059 (C—H, aromatic), 2926 (C—H, aliphatic). ^{1}H NMR (DMSO-d_6): 3.48 (s, 3H, N—CH_3), 3.74 (s, 3H, N—CH_3), 7.00—7.87 (m, 8H, aromatics). MS: m/z%: 354 [M^+, 24]. Anal. Calc. (%) for $C_{16}H_{14}N_6S_2$ (354.45): C, 54.22; H, 3.98; N, 23.71; S, 18.09. Found (%): C, 54.07; H, 3.89; N, 23.82; S, 17.84.

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