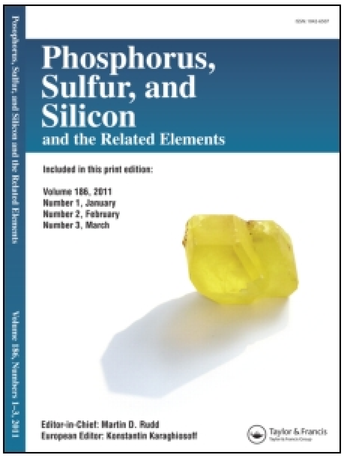


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

The Conversion of Stilbenols to Stilbenethiols *via* N,N-Dimethylthiocarbamates

Zdzisława Nowakowska[a]
[a] Department of Chemistry, Adam Mickiewicz University, Poznań, Poland

To cite this Article Nowakowska, Zdzisława(2006) 'The Conversion of Stilbenols to Stilbenethiols *via* N,N-Dimethylthiocarbamates', Phosphorus, Sulfur, and Silicon and the Related Elements, 181: 4, 707 — 715
To link to this Article: DOI: 10.1080/10426500500270016
URL: http://dx.doi.org/10.1080/10426500500270016

Phosphorus, Sulfur, and Silicon, 181:707–715, 2006

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500500270016

The Conversion of Stilbenols to Stilbenethiols *via* N,N-Dimethylthiocarbamates

Zdzisława Nowakowska
Department of Chemistry, Adam Mickiewicz University, Poznań, Poland

A series of O-stilbenyl N,N-dimethylthiocarbamates has been prepared by the reaction of N,N-dimethylthiocarbamoyl chloride with stilbenols in the presence of DABCO and DMF. The thermal rearrangement of O-stilbenyl N,N-dimethylthiocarbamates into S-stilbenyl analogues has also been studied. The S-stilbenyl N,N-dimethylthiocarbamates obtained have been converted into the corresponding stilbenethiols. Electron ionization mass spectral fragmentation of these compounds has been studied. Fragmentation pathways have been proposed on the basis of the accurate mass and metastable transition measurements.

Keywords EI-MS; Newman-Kwart rearrangement; stilbene

The thiol functionality is of prime importance in organic chemistry as well as in biochemistry. The conversion of phenols into the corresponding thiophenols is a very useful but not easy reaction. Since phenols are readily converted into the corresponding O-aryl dialkylthiocarbamates in a high yield by treatment with N,N′-dialkylthiocarbamoyl chloride and S-aryl dialkylthiocarbamates and are readily hydrolyzed to the corresponding aryl mercaptans, a general method is now available for the conversion of phenols to thiophenols.[1–7] The thermal rearrangement of O-aryl N,N-dimethylthiocarbamates to the S-aryl N,N-dimethylthiocarbamates proceeds by an intramolecular nucleophilic attack of the thiocarbonyl sulfur atom on the migrating aromating ring with a four-membered cyclic transition state, according to the Newman-Kwart rearrangement.[1,3] The rates of the rearrangement are much faster for the electron-withdrawing substituents than for the electron-releasing substituents. Although the rearrangement of many O-aryl dimethylthiocarbamates to the corresponding S-aryl compounds was successful, the following O-aryl analogs did not yield the

Received March 16, 2005; accepted April 15, 2005.

Address correspondence to Zdzisława Nowakowska, Adam Mickiewicz University, Department of Chemistry, Grunwaldzka 6, Poznań, 60-780 Poland. E-mail: zdzisian@main.amu.edu.pl

S-aryl compounds: aminophenyl, hydroxyphenyl, acetoxyphenyl, and acetylphenyl. In all these cases, decomposition set in well below the temperature needed for rearrangement.[1]

Stilbenes make a class of naturally occurring substances of great biological interest. Stilbenols isolated from different plants exhibit different pharmacological activity. They have been reported to exert estrogenic, fungistatic, antimicrobial, and antileukemic properties.[8–13] Resveratrol (3,5,4′-trihydroxy-*trans*-stilbene), found in grapes and wine, may play an active role in the prevention of heart disease and cancer. It has also been reported to exert antiestrogenic, antiinflammatory, antioxidant, and antiplatelet properties.

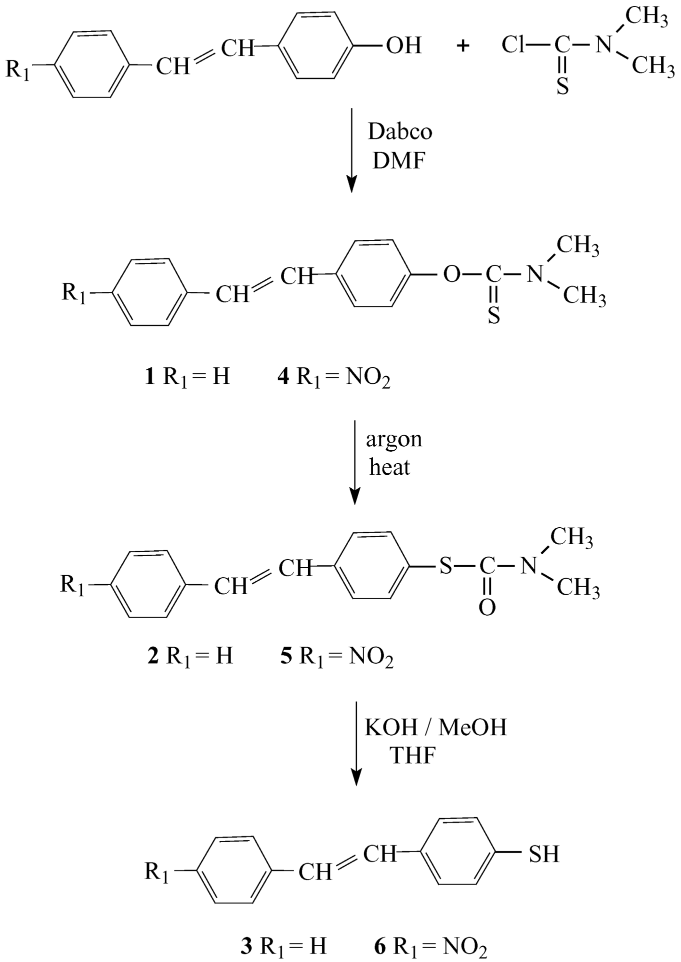
Although the reactions of the modifications of stilbenols as well as mass spectral[14–17] behavior of these compounds have been widely studied and interpreted, publications on mercapto analogues of these compounds have been rather limited. Thiolate anions are nucleophiles of theoretical and practical interest and are employed in a wide variety of organic reactions. They are usually generated in a solution by the treatment of the corresponding thiols with bases or sometimes by the basic hydrolysis of precursors such as thiol esters or other sulfur-containing compounds.

The purpose of this work is to establish an efficient and simple method of preparation of stilbenethiols. This article also presents mass spectrometric analyses of the obtained O-4-(and 4′-nitro-)stilbenyl N,N-dimethylthiocarbamates **1** and **4**, S-4-(and 4′-nitro-)stilbenyl N,N-dimethylthiocarbamates **2** and **5**, and 4-(and 4′-nitro-)stilbenethiols **3** and **6**, under Electron Impact (EI) ionization conditions, as well as metastable transitions and exact mass determinations of these compounds. The objective was to establish fragmentation pathways that may be of value in the structural determination of related compounds.

RESULTS AND DISCUSSION

O-stilbenyl N,N-dimethylthiocarbamates **1** and **4** used in the present study were synthesized by a reaction of *trans*-4-hydroxystilbene or *trans*-4′-nitro-4-hydroxystilbene with a commercially available N,N-dimethylthiocarbamoyl chloride in the presence of DABCO in refluxing dimethylformamide by the modifyed method of Newman and Karnes,[1,7] (Scheme 1).

The thermal rearrangement of the products O-4-stilbenyl and O-4-(4′-nitro-)stilbenyl N,N-dimethylthiocarbamates was investigated at temperatures of 270°C or 230°C in the absence of any solvent under a blanket of argon. The progress of the rearrangements was followed by changes in the ^{1}H NMR spectrum reflecting the transformation



1 $R_1 = H$ **4** $R_1 = NO_2$

2 $R_1 = H$ **5** $R_1 = NO_2$

3 $R_1 = H$ **6** $R_1 = NO_2$

SCHEME 1

of the two singlets assigned to the dimethylamino moiety of the O-stilbenyl thiocarbamate in the 3.37–3.42 ppm region into a broad singlet shifted upfield (to 3.02–3.05 ppm) assigned to the corresponding moiety of the S-aryl carbamates. The rearrangement reactions were confirmed by infrared spectra showing a disappearance of the strong absorptions in the mid-1540 cm^{-1} and mid-1280 cm^{-1} regions, characteristic of C=S bonds. However, the EI-MS spectral analysis seems to be the best way to check the extent of the rearrangement of O-aryl N,N-dimethylthiocarbamates to the S-aryl N,N-dimethylthiocarbamates. The lack of the m/z 88 ion peak $[C_3H_6NS]^+$ in the mass spectrum

TABLE I Elemental Composition and Relative Intensities of the Ion Peaks in the Spectra of 1–6 According to High-Resolution Data

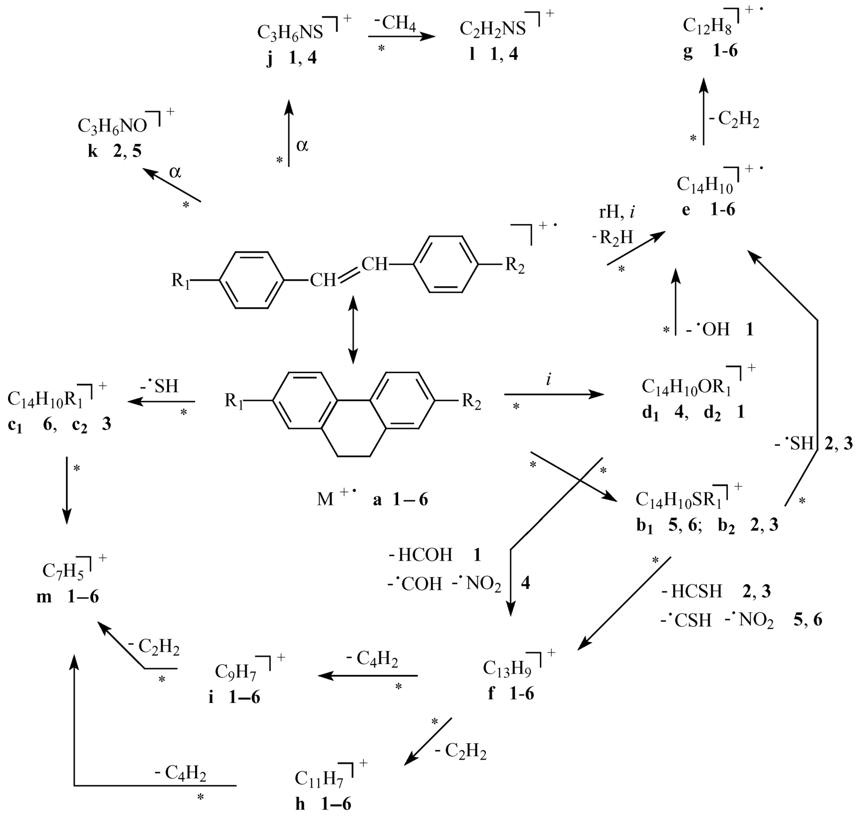
Ion	Elemental composition	m/z	Relative abundances % 1	2	3	4	5	6
	$C_{17}H_{17}NOS$	283	38.0	26.2	—	—	—	—
	$C_{14}H_{12}S$	212	—	—	100	—	—	—
a	$C_{17}H_{16}N_2O_3S$	328	—	—	—	16.4	5.9	—
	$C_{14}H_{11}NO_2S$	257	—	—	—	—	—	100
$\mathbf{b_1}$	$C_{14}H_{10}NO_2S$	256	—	—	—	—	1.2	4.2
$\mathbf{b_2}$	$C_{14}H_{11}S$	211	—	5.8	16.3	—	—	—
$\mathbf{c_1}$	$C_{14}H_{10}NO_2$	224	—	—	—	—	—	1.1
$\mathbf{c_2}$	$C_{14}H_{11}$	179	—	—	45.8	—	—	—
$\mathbf{d_1}$	$C_{14}H_{10}NO_3$	240	—	—	—	1.6	—	—
$\mathbf{d_2}$	$C_{14}H_{11}O$	195	3.5	—	—	—	—	—
e	$C_{14}H_{10}$	178	6.6	8.0	57.2	2.1	1.3	60.1
f	$C_{13}H_9$	165	13.8	6.6	11.5	14.0	5.7	29.6
g	$C_{12}H_8$	152	8.5	5.2	12.1	3.0	1.1	15.1
h	$C_{11}H_7$	139	3.6	2.5	4.2	4.5	1.1	6.5
i	C_9H_7	115	4.2	2.7	4.6	2.5	1.0	5.3
j	C_3H_6NS	88	100	—	—	92.0	—	—
k	C_3H_6NO	72	—	100	—	—	100	—
l	C_2H_2NS	72	95.8	—	—	100	—	—
m	C_7H_5	89	5.3	4.3	19.8	3.7	2.1	11.6

of the S-aryl derivatives **2** and **5** indicated that the rearrangement had occurred with a 100% yield.

On basic hydrolysis with potassium hydroxide dissolved in methanol, S-stilbenyl N,N-dimethylthiocarbamates afforded the corresponding arylthiols in high yield. Thus, the conversion of stilbenols into the thiophenolic analogs via the three-step procedure was highly successful.

On the basis of low- and high-resolution electron-ionization as well as B^2/E linked scan mass spectra, the principal mass spectral fragmentation routes of compounds **1–6** are interpreted as shown in Table I and Scheme 2. The O-C_{sp2} or S-C_{sp2} bond cleavage appeared to be the first step in the decomposition of the molecular ions in all compounds investigated.

In **1**, **2**, **4**, and **5** at the cleavage of S-C_{sp2} and O-C_{sp2} bonds the N,N-dimethylthiocarbamoyl substituent and two pairs of complementary ions (**b** and **k** as well as **d** and **j** even-electron fragment ions) are obtained. The molecular ions **a** of **1**, **2**, **4**, and **5** readily loose $C_{14}H_{10}R_1O^{\cdot}$ or $C_{14}H_{10}R_1S^{\cdot}$ radicals furnishing **k** or **j** even-electron fragment ions. The charge-site initiated inductive cleavages (i) proceed with the elimination of $^{\cdot}C(S)–N(CH_3)_2$ (**1**, **4**) or $^{\cdot}C(O)–N(CH_3)_2$ (**2**, **5**) radicals (even-electron fragment ions $\mathbf{d_1}$ or $\mathbf{d_2}$, and $\mathbf{b_1}$ or $\mathbf{b_2}$ are



Compound	R_1	R_2	Compound	R_1	R_2
1	H	O–C(S)–N(CH_3)$_2$	**4**	NO_2	O–C(S)–N(CH_3)$_2$
2	H	S–C(O)–N(CH_3)$_2$	**5**	NO_2	S–C(O)–N(CH_3)$_2$
3	H	SH	**6**	NO_2	SH

SCHEME 2 *Transitions checked by B^2/E spectra of compounds **1–6**.

obtained). The positive charge is stabilized more effectively on the $[C(S)–N(CH_3)_2]^+$ (**1**, **4**) and $[C(O)–N(CH_3)_2]^+$ (**2**, **5**) than on the stilbenyl fragment $[C_{14}H_{10}OR_1]^+$ (**1**, **4**) and $[C_{14}H_{10}SR_1]^+$ (**2**, **5**). Thus, for **1**, **2**, and **5**, the peaks of the ions **j** and **k** are the base peaks of the spectra. In the second step of the mass fragmentation of compounds **1** and **4**, the CH_4 molecule is eliminated from ions **j**, which leads to the final ions **l** of m/z 72. This fragmentation pathway was confirmed by metastable ion analyses and by exact mass measurements. In the linked scan B^2/E spectra of ion $[72]^+$, only ion $[88]^+$ was detected as its parent ion.

In the processes of the mass decomposition of the molecular ions, $M^{+\cdot}$ **a** of **1–6** is also observed the Mc Lafferty rearrangement, with a simultanous hydrogen transfer and elimination of R_2H neutral molecule. This decomposition produces the odd-electron fragment ion **e**. In the case of **1–3**, this ion is also formed by the inductive cleavage of the C_{sp2}-O or C_{sp2}-S bond in the even-electron fragment ions $\mathbf{d}_2$ and $\mathbf{b}_2$, with the ejection of the $^{\cdot}$OH as well as $^{\cdot}$SH radicals, respectively. The appearance of odd-electron ions **g** could be explained in terms of the elimination of C_2H_2 from odd-electron fragment ions **e** $[C_{14}H_{10}]^{+\cdot}$.

The even-electron fragment ions **f** $[C_{13}H_9]^+$ situated at m/z 165 were obtained by the elimination of the neutral molecule of formaldehyde from the fragment ion d_2 (**1**) or thioformaldehyde from fragment ions $\mathbf{b}_2$ (**2**, **3**). In the case of **4–6**, ions **f** are also obtained by the successive or simultaneous elimination of $^{\cdot}NO_2$ and $^{\cdot}$CSH or $^{\cdot}$COH radicals from even-electron fragment ions $\mathbf{b}_1$ (m/z 256) or d_1 (m/z 240).

The loss of the acethylene neutral molecule from the even-electron fragment ions **f** of **2** and **3** involves the formation of the even-electron fragment **h** (m/z 139). In the second step of the mass fragmentation, ion **f** decomposes by the ejection of the neutral molecule of C_4H_2 (even-electron fragment ion **i** is obtained). As follows from the B^2/E linked-scan spectra, the $[C_7H_5]^+$ ion **m** at m/z 89 is formed from three parent ions (even-electron ions **c**, **h**, and **i**).

In **3** and **6**, the mass fragmentation begins with the elimination of the $^{\cdot}$SH radical. By this fragmentation route, the c_1 and c_2 even-electron fragment ions are derived. These ions decompose further, giving even-electron fragment ions **m**. For structures **3** and **6**, the molecular ions $M^{+\bullet}$**a** (the base peaks in the mass spectra) lose also the $^{\cdot}$H radical, giving $\mathbf{b}_1$ or $\mathbf{b}_2$ even-electron fragment ions.

The UV/Vis spectra of all analyzed compounds **1–6** in chloroform contain two or three bands; most characteristic is an absorption maximum in the range of 314–319 nm (**1–3**) or 346–359 nm (**4–6**), and a second one shifted towards shorter wavelengths of 241–257 nm (**1–3**) or 240–253 nm (**4–6**). The presence of two distinct maxima at ~250 and ~320 or ~350 nm indicates typical $\pi \rightarrow \pi^*$ transitions of the conjugated system, which is corroborated by relatively high values of log ε.

The analysis of the IR spectra revealed (E)-configuration of the (E)-ethylene bridge of the stilbene skeletone for all studied compounds due to the presence of strong bands of out-of-plane *trans* olefinic C-H bending vibrations between 963–971 cm^{-1}. The IR spectra of **3** and **6** also show absorption bands of medium intensities in the region of 2440–2560 cm^{-1}, which have been assigned to the ν S-H vibrations. In the case of the NO_2 group, (**4–6**) gives intense absorption for symmetrical (~1340 cm^{-1}) and antisymmetrical (~1510 cm^{-1}) streching vibrations.

EXPERIMENTAL SECTION

General Remarks

The melting points were determined on a Melt-Temp II melting point apparatus and are uncorrected. Low- and high-resolution EI mass spectra were recorded using an AMD-Intectra GmbH (Harpstedt) D-27243 Model 402 two-sector mass spectrometer (ionizing voltage 70 eV, accelerating voltage 8 kV, resolution 1,000 for low-resolution and 10,000 for high-resolution mass spectra). Samples were introduced by a direct insertion probe at a source temperature of ∼50°C. The elemental compositions of all the ions discussed were determined by accurate mass measurement using a peak matching method relative to perfluorokerosene. All masses measured agreed with the compositions listed in column 2 of Table I to within ±2 ppm. The fragment ion spectra from the first field-free region, recorded using linked scans at constant B^2/E, with helium as the collision gas at a pressure of 1.73×10^{-5} mbar with an ion source temperature of 180°C, ionization energy of 70 eV and an accelerating voltage of 8 kV. Infrared spectra were recorded for KBr pellets on a Bruker IFS 113 FT-IR spectrometer. ^{1}H-NMR spectra were recorded on a Varian Gemini VT 300 spectrometer at 300.075 MHz using TMS as an internal standard, and $(CD_3)CO$ was used as a solvent. UV/VIS spectra were recorded on a Specord UV/VIS spectrophotometer in chloroform solution. Elemental analyses were performed on a Perkin-Elmer 240 CHN analyzer. All new compounds were analyzed for C, H, and N, and the results were in an acceptable range.

General Procedure for the Preparation of O-4- (and 4′-Nitro-)stilbenyl N,N-Dimethylthiocarbamates

To a solution of *trans*-4-hydroxystilbene (9.80 g, 50 mmol) [or *trans*-4′-nitro-4-hydroxystilbene (12.05 g, 50 mmol)] in dimethylformamide (80 mL), single portions of 1,4-diazabicyclo[2.2.2]octane (DABCO) (22.44 g, 200 mmol) and N,N-dimethylthiocarbamoyl chloride (12.36 g, 100 mmol) as solids were added. The resulting mixture was heated at 70°C for 3 h. After cooling, the salt was filtered off. The mixture was poured into 300 mL of ice-water and acidified to pH 3 with hydrochloric acid. The precipitate formed was filtered off, washed with 100 mL of water, and dried to yield a crude product. Recrystallization from a mixture of ethanol and water (3:1) provided 12.03 g (85%) pure O-4-stilbenyl N,N-dimethylthiocarbamate **1** and 14.27 g (87%) O-4-(4′-nitro-)stilbenyl N,N-dimethylthiocarbamate **4**.

1: m.p. 159–161°C; IR (KBr): 1539, 1501, 1393, 1287, 1203, 1132, 967 cm^{-1}; UV/Vis λ_{max}/nm 257, 302, 314; ^{1}H NMR 3.37 (3H, s, NCH_3), 3.41 (3H, s, NCH_3), 7.22 (1H, s, CH_α), 7.26 (1H, s, CH_β). Elemental Anal. Calcd. for $C_{17}H_{17}NOS$ (283): C, 72.08; H, 6.05; N, 4.95. Found: C, 72.01; H, 6.03; N, 4.90.

4: m.p. 232–233°C; IR (KBr): 1549, 1505, 1392, 1338, 1286, 969 cm^{-1}; UV/Vis λ_{max}/nm 253, 349; ^1H NMR 3.38 (3H, s, NCH_3), 3.42 (3H, s, NCH_3), 7.40 (1H, d, $J = 16.5$, CH_α), 7.56 (1H, d, $J = 16.5$, CH_β). Elemental anal. calcd. for $C_{17}H_{16}N_2O_3S$ (328): C, 62.18; H, 4.91; N, 8.54. Found: C, 62.08; H, 4.90; N, 8.51.

General Procedure for the Preparation of S-4- (and 4′-Nitro-)-stilbenyl N,N-Dimethylthiocarbamates

O-4-stilbenyl N,N-dimethylthiocarbamate (5.66 g, 20 mmol) [or O-4-(4′-nitro-)stilbenyl N,N-dimethylthiocarbamate (6.56 g, 20 mmol)] was placed into a 100-mL flask equipped with a reflux condenser and thermometer. The contents of the flask were maintained under argon for 0.5 h at 25°C, and then the flask was immersed in a preheated oil bath and heated at 270°C for **1** or 230°C for **4**. The reaction was complete in 2 h, yielding a single, clean rearranged product, S-4-(or 4′-nitro-)stilbenyl N,N-dimethylthiocarbamate. Upon cooling of the reaction mixture, the product crystallized in a quantitive yield. Recrystallization from a mixture of ethanol and water (3:1) provided 12.03 g (85%) of pure S-4-stilbenyl N,N-dimethylthiocarbamate **2** and 14.27 g (87%) of S-4-(4′-nitro-)stilbenyl N,N-dimethylthiocarbamate **5**.

2: m.p. 153–155°C; IR (KBr): 1668, 1495, 1362, 1259, 1088, 963 cm^{-1}; UV/Vis λ_{max}/nm 241, 307, 319; ^1H NMR 3.02 (6H, bs, $N(CH_3)_2$), 7.29 (2H, s, CH_α and CH_β). Elemental anal. calcd. for $C_{17}H_{17}OSN$ (283): C, 72.08; H, 6.05; N, 4.95. Found: C, 72.04; H, 6.03; N, 4.92.

5: m.p. 138–140°C; IR (KBr): 1671, 1595, 1515, 1342, 1088, 971 cm^{-1}; UV/Vis λ_{max}/nm 241, 272, 346; ^1H NMR 3.05 (6H, bs, $N(CH_3)_2$), 7.48 (1H, d, $J = 16.5$, CH_α), 7.57 (1H, d, $J = 16.5$, CH_β). Elemental anal. calcd. for $C_{17}H_{16}N_2O_3S$ (328): C, 62.18; H, 4.91; N, 8.54. Found: C, 62.03; H, 4.88; N, 8.50.

General Procedure for the Preparation of 4- (and 4′-Nitro-)-stilbenethiols

To a solution of the S-4-stilbenyl N,N-dimethylthiocarbamate (5.66 g, 20 mmol) [or S-4-(4′-nitro-)stilbenyl N,N-dimethylthiocarbamate (6.56 g, 20 mmol)] in tetrahydrofurane (90 mL), a portion of 10.5 mL of a methanol solution of potassium hydroxide (2.53 g, 45 mmol) was added. The reaction mixture was stirred at r.t. for 5 h and was then poured onto icewater and acidified with 6.0 N hydrochloric acid to attain a value of pH 3. The product was collected by filtration, washed with 100 mL of cold water, and recrystallized from ethanol and water (1:1) to give 3.67 g (87%) of pure 4-stilbenethiol **3** and 4.27 g (83%) of 4′-nitro-4-stilbenethiol **6**.

3: m.p. 135–137°C; IR (KBr): 2557, 1495, 1447, 1095, 969 cm^{-1}; UV/Vis λ_{max}/nm 241, 317; ^{1}H NMR 4.36 (1H, s, SH), 7.20 (2H, s, CH_α and CH_β). Elemental anal. calcd. for $C_{14}H_{12}S$ (212): C, 79.22; H, 5.70. Found: C, 79.20; H, 5.58.

6: m.p. 120–122°C; IR (KBr): 2447, 1584, 1507, 1336, 1103, 968 cm^{-1}; UV/Vis λ_{max}/nm 240, 276, 359; ^{1}H NMR 4.49 (1H, s, SH), 7.39 (1H, d, $J = 16.4$, CH_α), 7.50 (1H, d, $J = 16.5$, CH_β). Elemental anal. calcd. for $C_{14}H_{11}NO_2S$ (257): C, 65.36; H, 4.31; N, 5.45. Found: C, 65.34; H, 4.33; N, 5.53.

REFERENCES

[1] M. S. Newman and H. Karnes, *J. Org. Chem.*, **31,** 3980 (1966).

[2] H. M. Relles and G. Pizzolato, *J. Org. Chem.*, **33,** 2249 (1968).

[3] A. Kaji, Y. Araki, and K. Miyazaki, *Bull. Chem. Soc. Jpn.*, **44,** 1393 (1971).

[4] J. G. Samaritoni and G. E. Babbitt, *J. Heterocyclic Chem.*, **34,** 1263 (1997).

[5] M. Inouye, T. Miyake, M. Furusyo, and H. Nakazumi, *JACS*, **117,** 12416 (1995).

[6] D. Villemin, M. Hachemi, and M. Lalaoui, *Synth. Commun.*, **26,** 2461 (1996).

[7] S. Krishnamurthy and D. Aimino, *J. Org. Chem.*, **54,** 4458 (1989).

[8] T. P. Schultz, Q. Cheng, W. D. Boldin, T. F. Hubbard, L. Jin, T. H. Fisher, and D. D. Nicholas, *Phytochemistry*, **30,** 2939 (1991).

[9] T. P. Schultz, W. D. Boldin, T. H. Fisher, D. D. Nicholas, K. D. McMurtrey, and K. Pobanz, *Phytochemistry*, **31,** 3801 (1992).

[10] R. Kikumoto, A. Tobe, H. Fukami, K. Ninomiya, and M. Egawa, *J. Med. Chem.*, **27,** 645 (1984).

[11] Y. Inamori, M. Kubo, M. Ogawa, M. Moriwaki, H. Tsujibo, K. Baba, and M. Kozawa, *Chem. Pharm. Bull.*, **33,** 4478 (1985).

[12] L. -M. Yang, S.-J. Lin, F.-L. Hsu, and T. -H. Yang, *Bioorg. Med. Chem. Lett.*, **12,** 1013 (2002).

[13] H. Babich, A. G. Reisbaum, and H. L. Zuckerbraun, *Toxicology Letters*, **114,** 143 (2000).

[14] E. Wyrzykiewicz and D. Prukała, *Eur. J. Mass Spectrom.*, **5,** 183 (1999).

[15] P. Montoro, S. Piacente, W. Oleszek, and C. Pizza, *J. Mass Spectrom.*, **39,** 1131 (2004).

[16] E. Wyrzykiewicz, W. Prukała, and J. Grzesiak, *Org. Mass Spectrom.*, **25,** 181 (1990).

[17] U. Wannagat and R. Muenstedt, *Phosphorus, Sulfur, and Silicon*, **29,** 233 (1987).