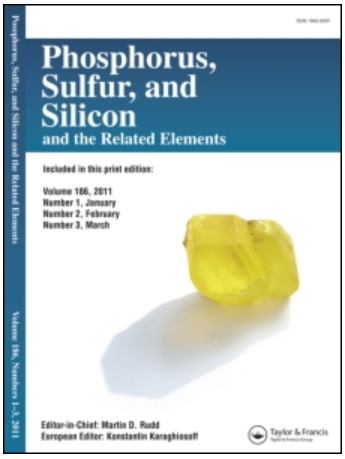

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Reactions of (E)-4-Stilbenethiole with Dibromoalkanes

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Reactions of (E)-4-Stilbenethiole with Dibromoalkanes

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New substituted stilbenes have been prepared by reactions of (E)-4-stilbenethiole with dibromoalkanes. ^{1}H and ^{13}C NMR spectra of new compounds have been assigned unambiguously on the basis of a combination of homo- ($^{1}H-^{1}H$ COSY) and heteronuclear ($^{1}H-^{13}C$ COSY-HETCOR) two-dimensional methods, chemical shifts, and spin-coupling constants.

Keywords Correlation techniques; coupling constant; ^{13}C NMR; ^{1}H NMR; stilbene

Since organic sulfur compounds have become increasingly useful and important in organic synthesis,[1] convenient preparations of appropriate sulfides, especially those that carry other functional groups, should be important. Stilbenols[2–11] make a class of naturally occurring substances of great biological interest. Although reactions of stilbenol modifications and physicochemical and biological behavior of these compounds have been widely studied and interpreted, publications on mercapto analogues of these compounds have been rare.[12–14]

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 treatment of the corresponding thiols with bases or sometimes by a basic hydrolysis of precursors, such as thiol esters or other sulfur-containing compounds.

In view of this fact, this article describes the influence of the reaction conditions on alkylation of (E)-4-stilbenethiole with dibromoalkanes. We have made attempts with the following bases: Na, NaOH, K_2CO_3, triethylamine and ethanol, methanol, DMF, and acetone as a solvents. The results are summarized in Figure 1.

In this work, a complete ^{1}H and ^{13}C signals assignment for substituted thiostilbenes was also achieved using ^{1}H-^{1}H correlation spectroscopy (COSY) and ^{1}H-^{13}C heteronuclear correlation (HETCOR)

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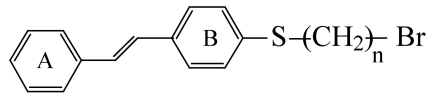

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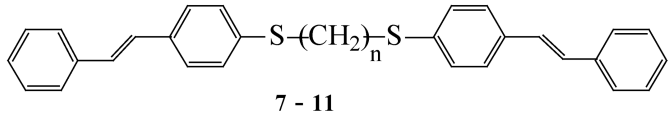

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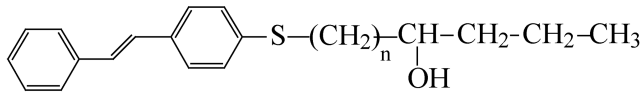

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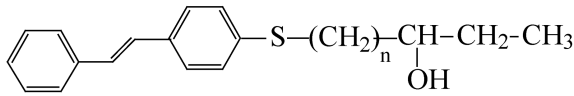

17 - 21

Compound	n	Compound	n	Compound	n	Compound	n
1	2	**7**	2	**12**	1	**17**	1
2	3	**8**	3	**13**	2	**18**	2
3	4	**9**	4	**14**	3	**19**	3
4	5	**10**	5	**15**	4	**20**	4
5	6	**11**	6	**16**	8	**21**	8
6	10						

FIGURE 1 Structures of compounds studied.

correlation experiments with chemical shifts and spin-coupling constants determined from ^{1}H NMR spectra. The COSY experiment was used in order to obtain structural information via spin connectivities revealed by cross peaks.

RESULTS AND DISCUSSION

(E)-4-bromoalkylthiostilbenes **1–6** were synthesized in 76–89% yields by a slow addition of a solution of (E)-4-stilbenethiole and triethylamine

TABLE I Chemical and Physical Data of Compounds 1–21

Compound	Molecular Formula (Mol. wt.)	M.P. (°C)	TLC R_f $CHCl_3$	IR (KBr, cm^{-1})
1	$C_{16}H_{15}SBr$ (319)	128–130	0.74	2928, 2856, 1587, 1495, 960
2	$C_{17}H_{17}SBr$ (333)	83–84	0.74	2925, 2855, 1588, 1498, 961
3	$C_{18}H_{19}SBr$ (347)	76–78	0.75	2921, 2855, 1589, 1495, 961
4	$C_{19}H_{21}SBr$ (361)	64–65	0.75	2927, 2857, 1589, 1495, 963
5	$C_{20}H_{23}SBr$ (375)	85–87	0.75	2931, 2854, 1590, 1497, 961
6	$C_{24}H_{31}SBr$ (431)	87–89	0.78	2921, 2855, 1588, 1495, 960
7	$C_{30}H_{26}S_2$ (450)	249–250	0.80	2925, 2850, 1590, 1497, 1248
8	$C_{31}H_{28}S_2$ (464)	181–183	0.79	2926, 2854, 1589, 1495, 1254
9	$C_{32}H_{30}S_2$ (478)	215–217	0.79	2926, 2852, 1590, 1495, 1244
10	$C_{33}H_{32}S_2$ (492)	168–169	0.80	2924, 2852, 1589, 1497, 1263
11	$C_{34}H_{34}S_2$ (506)	199–200	0.80	2924, 2853, 1590, 1496, 1269
12	$C_{19}H_{22}OS$ (298)	68–70	0.28	2933, 2855, 1496, 1114, 960
13	$C_{20}H_{24}OS$ (312)	70–71	0.29	2940, 2855, 1496, 1111, 960
14	$C_{21}H_{26}OS$ (326)	72–74	0.30	2935, 2850, 1495, 1110, 963
15	$C_{22}H_{28}OS$ (340)	72–73	0.33	2930, 2855, 1496, 1115, 960
16	$C_{26}H_{36}OS$ (396)	87–89	0.40	2930, 2854, 1495, 1119, 960
17	$C_{18}H_{20}OS$ (284)	68–69	0.39	2915, 2857, 1496, 1125, 961
18	$C_{19}H_{22}OS$ (298)	79–81	0.39	2916, 2859, 1495, 1126, 960
19	$C_{20}H_{24}OS$ (312)	78–79	0.38	2916, 2859, 1495, 1125, 963
20	$C_{21}H_{26}OS$ (326)	76–78	0.37	2919, 2858, 1497, 1126, 960
21	$C_{25}H_{34}OS$ (382)	85–87	0.39	2916, 2859, 1495, 1125, 962

in N,N-dimethylformamide to a solution of the corresponding dibromoalkane also in N,N-dimethylformamide. The r.t. and sequence of additions seemed to be key factors ensuring adequate reaction rates and minimal double substitutions.

When the reaction was performed in refluxing acetone in the presence of 0.005 molar equivalents of a basic solid, such as K_2CO_3, only (E)-4-bis-(stilbenylthio)alkanes **7–11** were obtained. The double displacement of bromine ions from dibromoalkanes was complete in 2 hours and gave excellent yields (92–96%).

Interestingly, (E)-4-stilbenethiol reacted with dibromoalkanes in a solution of sodium in absolute ethanol. In this method, (E)-4-(hydroxyalkylthio)stilbenes **12–16** were obtained in good yields (56–62%) with (E)-4-bis-(stilbenylthio)alkanes **8–11** as the second products in much lower yields.

For the sake of comparison, reactions were also performed in the homogeneous phase using a strong conventional base (NaOH) and methanol as a solvent. In this case, the amount of the base used up was 0.004 molar equivalents with respect to the amount of (E)-4-stilbenethiole. One of the major difficulties in carring out this reaction

was the formation of three types of products. Thus, this reaction led to a 25–39% yield of (E)-4-bromoalkylthiostilbenes **2–6** and a 13–19% yield of (E)-4-bis-(stilbenylthio)alkanes **8–11**. The most interesting products were (E)-4-(hydroxyalkyltio)stilbenes **17–21**, which were obtained in a yield of 44–53% (Table I).

The structural characterization of **1–21** was based on their spectral data (EI-MS[13], ^{1}H NMR, ^{13}C NMR, IR, UV/Vis) and elemental analysis.

The results of the extensive application of 1D (^{1}H NMR, ^{13}C NMR) and 2D (^{1}H-^{1}H COSY and ^{1}H-^{13}C HETCOR) correlation experiments were used to characterize the structures and to establish the ^{1}H and ^{13}C resonance assignments of these twenty one novel substituted thiostilbenes. The NMR data are given in Tables II–VII.

In the ^{13}C NMR spectra of substituted stilbenes **1–21**, differences in the chemical shifts of some carbons are very small (6 signals in the region 127–130 ppm were observed). To differentiate between the proton and carbon chemical shifts of ring A and those of ring B of compounds **1–21**, two dimentional techniques were employed.

It is interesting that in the ^{1}H NMR spectra of **1–21**, the chemical shifts at the ethylenic protons H_α and H_β give only one signal as a

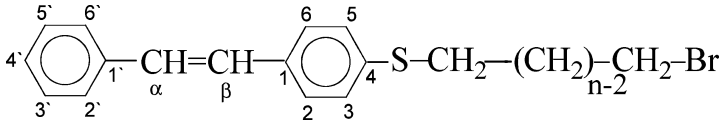

TABLE II ^{13}C NMR Spectral Data of Compounds 1–6

Carbon	1	2	3	4	5	6
Cα	128.86	128.46	127.65	127.61	127.59	127.79
Cβ	129.42	129.36	128.26	128.33	128.33	128.56
C-1	136.37	136.35	136.06	136.10	136.11	136.21
C-2,6	128.08	127.98	126.95	126.98	126.88	126.88
C-3,5	129.59	129.53	128.69	128.67	128.66	128.56
C-4	136.61	136.13	135.20	134.99	134.91	134.85
C-1′	138.43	138.32	137.17	137.08	137.20	137.29
C-2′,6′	127.39	127.35	126.45	126.48	126.42	126.27
C-3′,5′	130.10	130.01	129.31	128.86	128.96	128.79
C-4′	128.76	128.65	127.86	127.72	127.92	127.82
S-CH_2	32.83	32.85	32.75	33.55	33.35	33.40
CH_2-Br	32.95	32.99	33.03	33.54	33.78	33.98
$(CH_2)_{n-2}$	—	31.89	31.48	31.68	32.53	32.61; 29.94
			27.48	28.69	28.84	29.03; 28.56
				27.78	27.86	27.86; 27.81
					27.65	27.69; 27.57

TABLE III ^{1}H NMR Chemical Shifts (δ, ppm) and Coupling Constants (J, Hz) of 1–6

Compound	H-2′,6′ d, 2H	H-3′,5′ t, 2H	H-2,6 d, 2H	H-3,5 d, 2H	S-CH_2 t, 2H	CH_2-Br t, 2H	-CH_2- p, 2H
1	7.45	7.32	7.52	7.34	3.13	3.50	—
	(8.50)	(7.17)	(8.50)	(8.52)	(6.73)	(6.51)	
2	7.45	7.33	7.52	7.33	3.05	3.47	2.17
	(8.54)	(7.14)	(8.54)	(8.61)	(6.71)	(6.41)	
3	7.44	7.34	7.51	7.31	2.96	3.42	2.02
	(8.52)	(7.17)	(8.47)	(8.52)	(7.15)	(6.59)	1.84
4	7.44	7.35	7.50	7.29	2.95	3.41	1.99
	(8.50)	(7.17)	(8.60)	(8.61)	(7.14)	(6.60)	1.83; 1.68
5	7.43	7.35	7.49	7.29	2.93	3.40	1.85; 1.67
	(8.43)	(7.14)	(8.61)	(8.61)	(7.14)	(6.78)	1.46 m 4H
6	7.41	7.36	7.48	7.27	2.85	3.38	1.8–1.3 m
	(8.52)	(7.14)	(8.61)	(8.61)	(7.19)	(6.70)	16H

singlet (2H) at ~7.25 ppm for **1–11** and ~7.23 ppm for **12–21**. The one-bond coupling between the signals of the C_α and C_β with the ^{1}H NMR signal of the $H_{\alpha,\beta}$ allows a differentiation of these signals from those corresponding to the aromatic carbon atoms.

The ^{1}H NMR spectra of **1–6** revealed the presence of the CH_2-Br group characterized by the triplet signal at δ_H 3.38–3.50 ppm. These signals were correlated with the ^{13}C chemical shifts at δ_C 32.95–33.98, respectively, in the ^{1}H-^{13}C HETCOR spectrum.

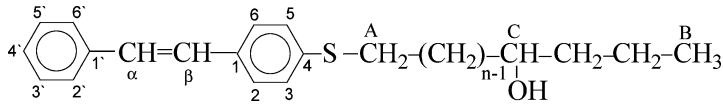

TABLE IV ^{13}C NMR Spectral Data of Compounds 12–16

Carbon	**12**	**13**	**14**	**15**	**16**
Cα	128.39	128.37	128.35	128.24	128.13
Cβ	129.07	129.03	128.98	128.98	128.68
C-1	137.24	137.26	137.44	137.38	137.18
C-2,6	127.88	127.85	127.82	127.73	127.65
C-3,5	129.39	129.36	129.33	129.38	129.26
C-4	135.87	135.86	135.76	135.76	135.58
C-1′	138.38	138.35	138.34	138.28	138.12
C-2′,6′	127.32	127.30	127.28	127.19	127.04
C-3′,5′	129.53	129.51	129.50	129.41	129.31
C-4′	128.76	128.76	128.74	128.71	128.69
A	36.88	36.88	33.41	33.67	33.09
B	15.54	15.54	15.55	15.63	15.60
C	69.14	69.83	70.78	70.86	70.99

TABLE V ^{1}H NMR Chemical Shifts (δ, ppm) and Coupling Constants (J, Hz) of 12–16

Compound	H-2′,6′ d, 2H	H-3′,5′ t, 2H	H-2,6 d, 2H	H-3,5 d, 2H	A t, 2H	B t, 3H	C m, 1H	OH bs, 1H
12	7.59 (8.54)	7.36 (7.14)	7.55 (8.54)	7.35 (8.08)	2.88 dd 1H 3.06 dd 1H	1.14 (7.14)	3.51	2.96
13	7.58 (8.52)	7.36 (7.14)	7.55 (8.54)	7.35 (8.54)	3.03 (7.02)	1.12 (7.14)	3.48	2.95
14	7.59 (8.23)	7.37 (7.14)	7.55 (8.58)	7.34 (8.24)	3.00 (7.14)	1.12 (7.14)	3.42	2.95
15	7.59 (8.52)	7.37 (7.14)	7.55 (8.52)	7.34 (8.52)	2.99 (7.14)	1.11 (7.14)	3.36	2.95
16	7.59 (8.50)	7.35 (7.14)	7.55 (8.52)	7.33 (8.24)	2.97 (7.14)	1.10 (7.14)	3.37	2.95

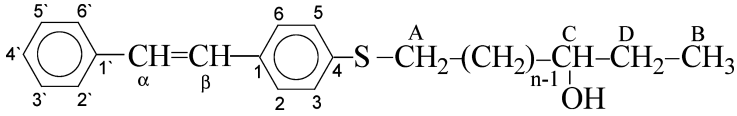

TABLE VI ^{13}C NMR Spectral Data of Compounds 17–21

Carbon	**17**	**18**	**19**	**20**	**21**
Cα	128.32	128.23	128.38	128.46	128.44
Cβ	128.91	128.89	128.93	129.09	1289.08
C-1	137.17	137.19	137.32	137.57	137.49
C-2,6	127.73	127.72	127.88	127.93	127.90
C-3,5	129.23	129.24	129.41	129.46	129.26
C-4	135.69	135.67	135.77	135.88	135.80
C-1′	138.30	138.22	138.26	138.47	138.39
C-2′,6′	127.20	127.16	127.28	127.39	127.30
C-3′,5′	129.39	129.37	129.51	129.60	129.53
C-4′	128.65	128.63	128.70	128.86	128.68
A	33.94	33.34	33.23	33.51	33.28
B	26.82	26.79	26.69	26.53	26.50
C	72.49	72.51	72.86	73.13	73.22
D	29.51	29.43	29.38	29.32	29.29

In the NMR spectra of (E)-4-bis-(stilbenylthio)alkanes (**7–11**), the triplet at δ 2.98–3.21 ppm corresponding to the S-CH_2 protons integrating for 4 protons fully supported the respective structures. These signals showed coupling to carbons at δ 32.20–32.44 ppm. In general, the proton and carbon signals of the aromatic rings of **7–11** were observed in the same range as for (E)-4-bromoalkylthiostilbenes (**1–6**).

TABLE VII ^{1}H NMR Chemical Shifts (δ, ppm) and Coupling Constants (J, Hz) of 17–21

Compound	H-2′,6′ d, 2H	H-3′,5′ t, 2H	H-2,6 d, 2H	H-3,5 d, 2H	A t, 2H	B t, 3H	C m, 1H	OH bs, 1H
17	7.59 (7.14)	7.37 (7.14)	7.55 (8.51)	7.33 (8.51)	2.81 dd 1H 3.15 dd 1H	1.69 (7.14)	3.38	3.15
18	7.59 (7.14)	7.37 (7.14)	7.55 (8.51)	7.33 (8.51)	2.96 (7.14)	1.69 (7.14)	3.39	3.15
19	7.59 (7.14)	7.37 (7.14)	7.55 (8.51)	7.33 (8.51)	2.96 (7.14)	1.69 (7.14)	3.42	3.15
20	7.59 (7.11)	7.40 (7.11)	7.55 (8.55)	7.30 (8.53)	2.99 (7.14)	1.43 (7.14)	3.37	3.15
21	7.59 (7.14)	7.37 (7.14)	7.55 (8.51)	7.33 (8.51)	2.96 (7.14)	1.69 (7.14)	3.39	3.13

The ^{1}H NMR spectra of **12–21** exhibit a signal assigned to the proton at the carbon connected to the OH group. The signal appears at 3.36–3.51 ppm for (**12–16**) and 3.37–3.42 ppm for (**17–21**). In their ^{13}C NMR spectra, these compounds show the signal assigned to C-OH at 69.14–70.99 ppm for **12–16** and at 72.49–73.22 ppm for **17–21**, respectively. Finally, the OH proton appears as a broad singlet in all cases at ~2.95–3.15 ppm.

The UV/V is spectra of all analyzed compounds in chloroform contain 2 to 3 bands; the most characteristic is the absorption maximum in the range of 240.5–241.5 nm, and another one shifted toward longer wavelengths of $321.5 \leq \lambda_{max} \leq 323.0$ nm. The presence of two distinct maxima at 240 and 320 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 the (E)-configuration of the ethylene bridge of the stilbene skeletone due to the presence of strong bands of out-of-plane *trans* olefinic C-H bending vibrations between 960–963 cm^{-1}. The IR spectra of **1–21** show also absorption bands of medium intensities in the region 2830–2940 cm^{-1} assigned to ν C-S vibrations. IR measurements of the (E)-4-(hydroxyalkylthio)stilbenes **12–21** showed C-O stretching frequency at 1110–1127 cm^{-1}.

EXPERIMENTAL SECTION

General Remarks

Melting points were determined on a Melt-Temp II melting point apparatus and are uncorrected. Infrared spectra were recorded for KBr

pellets on a Bruker IFS 113 FTIR spectrometer. All 1D and 2D NMR spectra were recorded at r.t. on a Varian Mercury 300 spectrometer operating at 75.462 MHz for ^{13}C and 300.071 MHz for ^{1}H. Spectra were measured in $CDCl_3$ for **1–11** and $(CD_3)_2CO$ for **12–21** (~10 mg of the sample were dissolved in 0.5 mL of the solvent and transferred into a 5-mm NMR tube) with TMS (tetramethylsilane) as an internal standard. ^{1}H NMR spectra were recorded with a spectral width of 9 kHz, an acquisition time of 3.5 s, a pulse width of 6.0 μs, and a double precision acquisition. The ^{13}C NMR spectra were recorded with a spectral width of 23 kHz, an acquisition time of 1.5 s, a recycle delay of 1.0 s, and a pulse width of 8.0 μs. The homonuclear ^{1}H-^{1}H shift-correlated two-dimensional diagrams were obtained using the COSY pulse sequence. The spectral width was 3.05 kHz; there was a relaxation delay of 1 s, number of increments in t_1 256, and 16 scans. The heteronuclear 2D ^{1}H-^{13}C chemical shift correlation experiments were carried out using HETCOR spectra. Spectra were acquired with 2,048 data points in the F_2 dimension and 256 increments in the F_1 dimension. Increments were obtained using 128 scans and a relaxation delay of 1 s. The spectral width was 15 kHz in the F_2 and 3.2 kHz in the F_1 dimension. UV/VIS spectra were recorded on a Specord UV/VIS spectrophotometer in a chloroform solution. Elemental analyses were performed on a Perkin-Elmer 240 CHN analyzer. All new compounds were analyzed for C, H, and S, and satisfactory results were obtained.

General Procedure for the Preparation of (E)-4-bromoalkylthiostilbenes 1–6

To a solution of 0.002 mole of corresponding dibromoalkane in 2 mL of N,N-dimethylformamide, a solution consisting of 0.212 g (0.001 mol) of (E)-4-stilbenethiole in 8 mL of dimethylformamide and 0.32 mL (0.002 mol) of triethylamine was added. The reaction mixture was stirred at r.t. for 3 h, was diluted with an ethanol-water (20–30 mL) mixture, and was allowed to stand for 24 h. The solid formed was filtered off, dried, and recrystallized from ethanol to yield products **1–6**.
Anal. calcd. for **1** $C_{16}H_{15}SBr$: C, 60.17; H, 4.74; S, 10.05. Found: C, 60.09; H, 4.70; S, 10.02.
Anal. calcd. for **2** $C_{17}H_{17}SBr$: C, 61.24; H, 5.14; S, 9.62. Found: C, 61.21; H, 5.18; S, 9.57.
Anal. calcd. for **3** $C_{18}H_{19}SBr$: C, 62.22; H, 5.52; S, 9.23. Found: C, 62.18; H, 5.47; S, 9.19.
Anal. calcd. for **4** $C_{19}H_{21}SBr$: C, 63.13; H, 5.86; S, 8.78. Found: C, 63.02; H, 5.89; S, 8.65.

Anal. calcd. for **5** $C_{20}H_{23}SBr$: C, 63.97; H, 6.13; S, 8.55. Found: C, 63.91; H, 6.10; S, 8.54.
Anal. calcd. for **6** $C_{24}H_{31}SBr$: C, 66.78; H, 7.18; S, 7.43. Found: C, 66.79; H, 7.72; S, 7.38.

General Procedure for the Preparation of (E)-4-bis-(stilbenylthio)alkanes 7–11

A mixture of (E)-4-stilbenethiole (0.212 g, 0.001 mol), dibromoalkane (0.002 mol), K_2CO_3 (0.69 g, 0.005 mol) and anhydrous acetone (20 mL) was refluxed for 2–2.5 h, and the inorganic salts were filtered off. The residue was cooled and left for 24 h. The precipitated solid was filtered off, washed with warm ethanol, and dried. Using this method, products **17–11** were obtained.
Anal. calcd. for **7** $C_{30}H_{26}S_2$: C, 79.97; H, 5.82; S, 14.21. Found: C, 79.91; H, 5.76; S, 14.14.
Anal. calcd. for **8** $C_{31}H_{28}S_2$: C, 80.14; H, 6.08; S, 13.82. Found: C, 80.19; H, 6.02; S, 13.80.
Anal. calcd. for **9** $C_{32}H_{30}S_2$: C, 80.30; H, 6.32; S, 13.37. Found: C, 80.28; H, 6.28; S, 13.30.
Anal. calcd. for **10** $C_{33}H_{32}S_2$: C, 80.46; H, 6.55; S, 12.99. Found: C, 80.43; H, 6.51; S, 12.89.
Anal. calcd. for **11** $C_{34}H_{34}S_2$: C, 80.92; H, 6.40; S, 12.68. Found: C, 80.88; H, 6.32; S, 12.62.

General Procedure for the Preparation of (E)-4-(hydroxyalkylthio)stilbenes 12–16

A mixture of Na (0.23 g, 0.01 mol) in 30 mL of ethanol, (E)-4-stilbenethiole (0.212 g, 0.001 mol), and dibromoalkane (0.002 mol) was refluxed for 4 h. The precipitated solids were filtered off while still hot. The obtained crude products were analyzed as (E)-4-bis-(stilbenylthio)alkanes **8–11**. After filtration, the reaction mixture was then concentrated to ca. half the original volume on a rotary evaporator. The precipitated solid was filtered off, dried, and recrystallized from an ethanol-water mixture to afford crystaline products of **12–16**.
Anal. calcd. for **12** $C_{19}H_{22}OS$: C, 76.47; H, 7.44; S, 10.75. Found: C, 76.41; H, 7.40; S, 10.77.
Anal. calcd. for **13** $C_{20}H_{24}OS$: C, 76.88; H, 7.75; S, 10.24. Found: C, 76.79; H, 7.69; S, 10.20.
Anal. calcd. for **14** $C_{21}H_{26}OS$: C, 77.26; H, 8.03; S, 9.80. Found: C, 77.23; H, 7.98; S, 9.82.

Anal. calcd. for **15** $C_{22}H_{28}OS$: C, 77.60; H, 8.29; S, 9.43. Found: C, 77.58; H, 8.24; S, 9.37.
Anal. calcd. for **16** $C_{26}H_{36}OS$: C, 78.74; H, 9.16; S, 8.07. Found: C, 78.70; H, 9.04; S, 8.01.

General Procedure for the Preparation of (E)-4-(hydroxyalkylthio)stilbenes 17–21

To a solution of 0.212 g (0.001 mol) of (E)-4-stilbenethiole in 40 mL of 0.1 N NaOH/MeOH, a solution of 0.002 mol of the corresponding dibromoalkane was added. The reaction mixture was refluxed for 20 min, and the precipitated solid was filtered off while still hot (products **8–11**). After filtration, the solvent was evaporated an a rotary evaporator, and the residue was separated on a silica gel column (Merck, 63–100 mesh) using chloroform as an eluent. Fractions of 10 mL were collected and monitored by analytical TLC. The (E)-4-bromoalkylthiostilbenes **2–6** were obtained from fractions 4–5. The desired products **17–21** were obtained from fractions 8–10.
Anal. calcd. for **17** $C_{18}H_{20}OS$: C, 76.02; H, 7.09; S, 11.28. Found: C, 75.94; H, 7.11; S, 11.23.
Anal. calcd. for **18** $C_{19}H_{22}OS$: C, 76.47; H, 7.44; S, 10.75. Found: C, 76.41; H, 7.38; S, 10.76.
Anal. calcd. for **19** $C_{20}H_{24}OS$: C, 76.88; H, 7.75; S, 10.24. Found: C, 76.81; H, 7.65; S, 10.15.
Anal. calcd. for **20** $C_{21}H_{26}OS$: C, 77.26; H, 8.03; S, 9.80. Found: C, 77.20; H, 7.92; S, 9.72.
Anal. calcd. for **21** $C_{15}H_{34}OS$: C, 78.48; H, 8.96; S, 8.39. Found: C, 78.49; H, 8.96; S, 8.37.

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