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2-(1*H*-Benzotriazol-1-ylmethyl)-1-naphthalenol (**1**) can be transformed in high yields to the corresponding thiol **4**. Flash vacuum pyrolysis of **4** leads to 2*H*-naphtho[1,2-*b*]thiete (**5**). The benzotriazolyl group proved to be a good leaving group; however, a subsequent nitrogen extrusion takes place under flash vacuum pyrolysis conditions and cyclopentadienecarbonitriles **6a,b** are formed by a ring contraction (Scheme 1). Cycloaddition reactions of **5** and dienophiles or heterodienophiles yield the naphtho-condensed sulfur heterocycles **8**, **10**, **12** and **14** (Scheme 2).

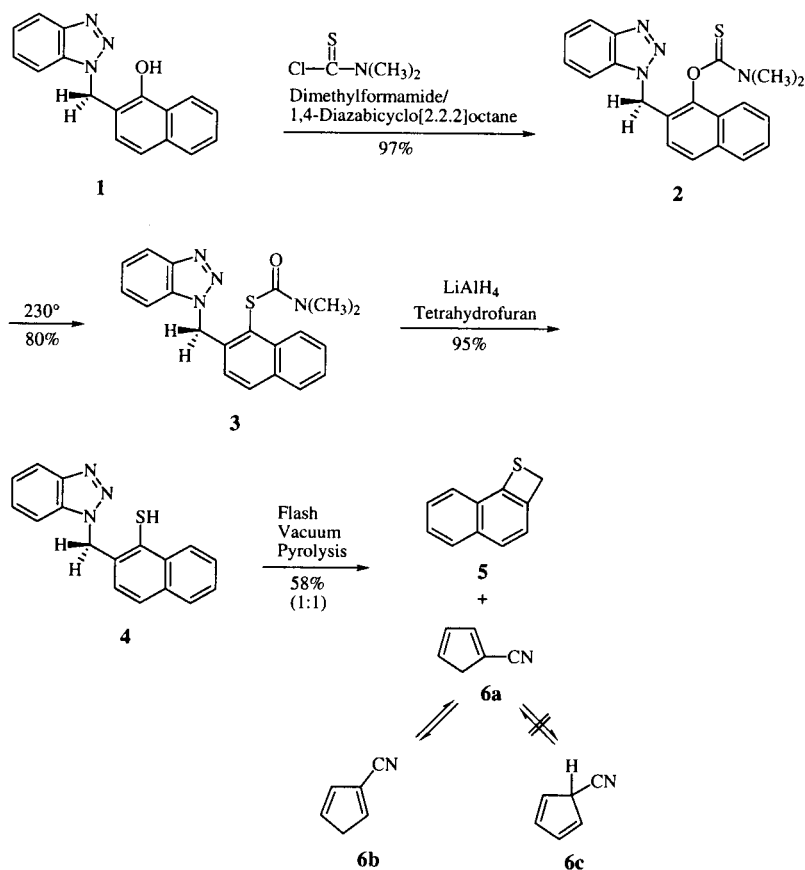
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Areno-condensed thietes represent very versatile reagents for the preparation of a variety of sulfur heterocycles [1,2]. The usual synthesis of the thiete ring consists of the 1,4-elimination of water from *o*-hydroxymethylthiols [1]. A flash vacuum pyrolysis technique has to be applied for this purpose. In an alternative process the hydroxy-

methylthiol is first transformed by the reaction with trichloromethyl chloroformate to the corresponding 1,3-oxathiin-2-one; then a decarboxylation by a thermolysis in refluxing toluene or xylene yields the desired thiete [3].

o-Hydroxymethylthiols tend to undergo *intermolecular* condensation reactions which lower the yield of the

Scheme 1



intramolecular process. In order to avoid these side reactions we introduced the benzotriazolyl group as the leaving group. 2-(1*H*-Benzotriazol-1-ylmethyl)-1-naphthalenol (**1**) [4] was treated with *N,N*-dimethylthiocarbamoyl chloride in dimethylformamide/1,4-diazabicyclo[2.2.2]octane. The *O*-ester **2** of *N,N*-dimethylthiocarbamic acid was obtained in an almost quantitative yield. Newman-Kwart rearrangement [5,6] led to the corresponding *S*-ester **3** which was reduced with lithium aluminum hydride to the naphthalenethiol **4**. Flash vacuum pyrolysis at 750° and $5.0 \cdot 10^{-5}$ Torr yielded the expected 2*H*-naphtho[1,2-*b*]thiete (**5**). 1*H*-Benzotriazole was eliminated from **4**; however, under the flash vacuum pyrolysis conditions applied, benzotriazole extruded molecular nitrogen and underwent a subsequent ring contraction to generate 1-cyclopentadienecarbonitrile (**6a**) and its isomer **6b**. A suprafacial 1,5-H-shift could

also lead to the isomer **6c**, but **6c** could not be detected in the equilibrium. This result corresponds to the well-known pyrolysis of 1*H*-benzotriazole [7,8]. Other products would be expected, should the nitrogen extrusion occur prior to the N-CH₂ cleavage in **4** [9]. Compound **5** is identical with the product obtained earlier by flash vacuum pyrolysis of 1-mercapto-2-naphthalenemethanol [10,11].

The synthetic intermediates **2**, **3** and **4** were characterized by ¹H nmr, ¹³C nmr and mass spectra (Experimental). The proton resonance shows a remarkable effect for the methylene group which bears - depending on the steric influence - enantiotopic or diastereotopic protons (Table 1).

The naphthothiete **5** can be used for various cycloaddition reactions. Facile thermal opening of the 4-membered ring confers on **5** the character of a heterodiene. We

Scheme 2

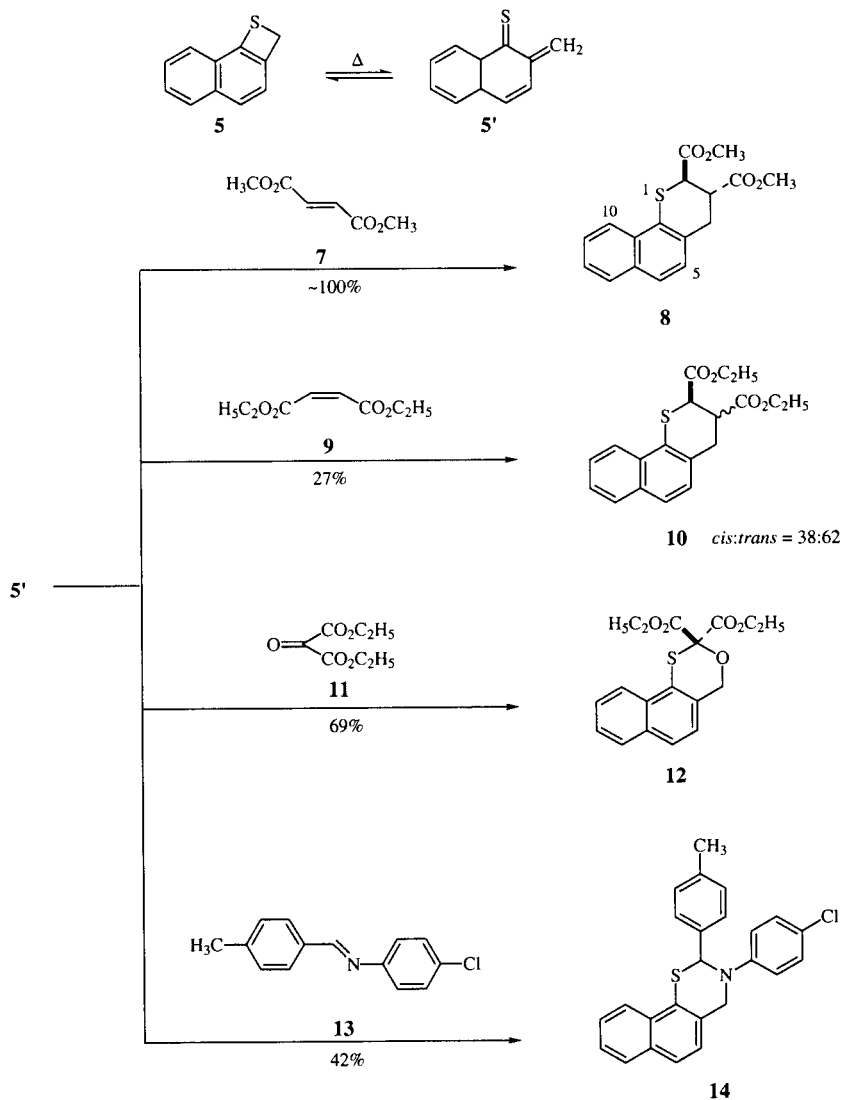


Table 1

¹H and ¹³C NMR Signals of the CH₂ Groups in **1-4** and **6** (measured in deuteriochloroform versus tetramethylsilane as internal standard)

Compound	δ(¹ H)	Spin system	δ(¹³ C)
1	6.08	A ₂ singlet	46.1
2	5.81/6.10	AB system with ² J = -15.8 Hz	48.4
3	6.29	(AB) broad singlet	51.4
4	6.20	A ₂ singlet	51.6
6	4.40	A ₂ singlet	36.3

reacted **5** with fumaric and maleic diesters **7** and **9** as dienophiles and with mesoxalic diethyl ester (**11**) and *N*-(4-chlorophenyl)-4-methylbenzaldimine (**13**) as heterodienophiles.

Maleates are much less reactive than fumarates. Additionally maleates show a lack of stereoselectivity. Diester **9** led in a non-concerted reaction to a mixture of stereoisomers: *cis*-**10**: *trans*-**10** = 38:62 [12]. An isomerization was excluded at the stage of the olefin **9**, as well as in the product **10**.

EXPERIMENTAL

Melting points were taken on a Büchi melting point apparatus. The ¹H and ¹³C nmr spectra were run on Bruker AM 400 and AC 200 spectrometers in deuteriochloroform. The mass spectra were recorded on a Finnigan M 95. 2-(1*H*-Benzotriazol-1-ylmethyl)-1-naphthalenol (**1**) was prepared according to the literature [4].

2-(1*H*-Benzotriazol-1-ylmethyl)naphth-1-yl *N,N*-Dimethyl-*O*-thiocarbamate (**2**).

2-(1*H*-Benzotriazol-1-ylmethyl)-1-naphthalenol (**1**) (1.10 g, 4.0 mmoles), *N,N*-dimethylthiocarbamoyl chloride (1.484 g, 14.8 mmoles) and 1,4-diazabicyclo[2.2.2]octane (1.346 g, 13.0 mmoles) were stirred in 50 ml of dimethylformamide under argon at room temperature. After 12 hours the mixture was poured into 50 ml of water, stirred for 1 hour and the resinous residue dissolved in 100 ml of toluene and dried over magnesium sulfate. Evaporation at 1 Torr and room temperature yielded the oily ester **2** (1.40 g, 97%) which solidified below 5°. It showed ¹H nmr signals at δ 3.36 (s, 3 H, CH₃), 3.50 (s, 3 H, CH₃), 5.81/6.10 (AB, ²J = -5.8 Hz, 2 H, CH₂), 7.16-8.05 (m, 10 H, aromatic H), and ¹³C nmr signals at δ 38.8 (CH₃), 43.6 (CH₃) 48.4 (CH₂), 110.1/ 119.7/ 121.7/ 124.2/ 125.3/ 126.8/ 126.9/ 127.1/ 127.4/ 128.1 (10 aromatic CH), 124.3/ 127.6/ 133.2/ 134.5/ 145.9/ 147.6 (6 aromatic Cq), 186.0 (CS). The EI ms spectrum measured at 70 eV showed peaks at *m/z* (%) 362 (7) [M⁺], 172 (23), 91 (15), 88 (18), 72 (100).

Anal. Calcd. for C₂₀H₁₈N₄OS: C, 66.28; H, 5.01; N, 15.53. Found: C, 66.09; H, 5.17; N, 15.53.

2-(1*H*-Benzotriazol-1-ylmethyl)naphth-1-yl *N,N*-Dimethyl-*S*-thiocarbamate (**3**).

Compound **2** (1.31 g, 3.6 mmoles) was heated in 40 ml of diphenyl ether under argon for 1-2 hours to 230°. After vacuum

evaporation (1 Torr) of the solvent, the residue was dissolved in toluene. Column chromatography (50 x 2 cm silica gel, toluene) yielded the oily ester **3** (1.05 g, 80%) which showed ¹H nmr signals at δ 3.00 (s, 3 H, CH₃), 3.30 (s, 3 H, CH₃), 6.29 (br s, 2 H, CH₂), 7.02-8.52 (m, 10 H, aromatic H), and ¹³C nmr signals at δ 37.2 (2 CH₃), 51.4 (CH₂), 110.4/ 119.7/ 124.1/ 124.9/ 126.0/ 126.6/ 127.5/ 127.6/ 128.5/ 131.3 (10 aromatic CH), 128.2/ 133.2/ 133.6/ 135.6/ 138.9/ 146.0 (6 aromatic Cq), 164.5 (CO). In the EI ms spectrum (70 eV) peaks were observed at *m/z* (%) 362 (1) [M⁺], 119 (26), 92 (68), 91 (100).

Anal. Calcd. for C₂₀H₁₈N₄OS: C, 66.28; H, 5.01; N, 15.53. Found: C, 66.19; H, 5.12; N, 15.53.

2-(1*H*-Benzotriazol-1-ylmethyl)-1-naphthalenethiol (**4**).

The ester **3** (1.0 g, 2.76 mmoles) dissolved in 50 ml of dry tetrahydrofuran was slowly added under argon at 0° to a suspension of 315 mg (8.3 mmoles) lithium aluminum hydride in 25 ml of dry tetrahydrofuran. After an additional hour stirring at room temperature 25 ml of water and 12.5 ml of 3% hydrochloric acid were added slowly. The reaction mixture was extracted with 3 x 100 ml ether. The organic phase was dried over magnesium sulfate and concentrated. Pale yellow crystals (764 mg, 95%) precipitated, which melted at 105° and showed ¹H nmr signals at δ 3.72 (s, 1 H, SH), 6.20 (s, 2 H, CH₂), 7.12-8.42 (m, 10 H, aromatic H) and ¹³C nmr signals at δ 51.6 (CH₂), 109.9/ 120.0/ 124.2/ 125.9/ 125.9/ 126.8/ 127.4/ 127.6/ 128.3/ 128.6 (10 aromatic CH), 126.6/ 133.0/ 133.4/ 133.4/ 133.8/ 146.1 (6 aromatic C_q). The EI ms spectrum (70 eV) showed peaks at *m/z* (%) 291 (53) [M⁺], 263 (24), 262 (100), 258 (13), 247 (13), 230 (56), 186 (15), 173 (28), 172 (55), 171 (37).

Anal. Calcd. for C₁₇H₁₃N₃S: C, 70.08; H, 4.50. Found: C, 69.89; H, 4.56.

2*H*-Naphtho[1,2-*b*]thieth (**5**).

Compound **4** (291 mg, 1.0 mmole) was pyrolyzed in a quartz vessel (100 x 3 cm) at 750° and 5.0•10⁻⁵ Torr. The vapor flow was about 10 mg/hour. The trap cooled with liquid nitrogen contained 156 mg of the products; according to the ¹H nmr spectrum it was a 50:50 mixture of **5** and the cyclopentadienecarbonitriles **6a,b** [7,8]. Due to the high volatility **6a,b** could be evaporated at ambient temperatures in the high vacuum. The identification of **5** (100 mg, 58%), which melted at 37°, was by comparison with an authentic sample [10,11].

General Procedure for the Cycloaddition Reactions of 2*H*-Naphtho[1,2-*b*]thieth (**5**).

The naphthothiete **5** (110 mg, 0.64 mmole) and 0.70 mmole of dienophiles **7**, **9**, **11**, or **13** were dissolved in 30 ml of dry toluene. The solution was refluxed for 1 to 4 hours, and the course of the reactions controlled by tlc. After complete consumption of **5** the toluene was evaporated under reduced pressure. The resulting residue was dissolved in dichloromethane and purified by column chromatography (15 cm x 4 cm silica gel).

trans-Dimethyl 2*H*-3,4-Dihydronaphtho[1,2-*b*]thiopyran-2,3-dicarboxylate (**8**).

A quantitative yield (202 mg) of **8** was isolated [3]. The colorless crystals melted at 108° and were identified by comparison with an authentic sample. The NOE measurements led to the exact correlation of the ¹H nmr signals at δ 3.11 (dd, 1 H, 4-H), 3.32 (dd, 1 H, 4-H), 3.39 (m, 1 H, 3-H), 3.74 (s, 3 H, CH₃), 3.77 (s, 3 H, CH₃), 4.49 (d, 1 H, 2-H), 7.23 (d, 1 H, 5-H), 7.47 (m, 2

H, 8-H, 9-H), 7.58 (m, 1 H, 6-H), 7.77 (m, 1 H, 7-H), 8.09 (m, 1 H, 10-H).

cis/trans-Diethyl 2*H*-3,4-Dihydronaphtho[1,2-*b*]thiopyran-2,3-dicarboxylate (**10**).

Diethyl maleate (**9**) (121 mg, 0.70 mmole) and **5** (110 mg, 0.64 mmole) yielded after purification by chromatography with light petroleum/ethyl acetate with a gradient from 40:1 to 10:1 an oil (59 mg, 27%). According to the ¹H nmr spectrum in deuteriochloroform it consisted of a 38:62 *cis/trans* mixture of **10**. It showed signals for *trans*-**10** at δ 1.26 (t, 6 H, 2 CH₃), 3.09 (dd, 1 H, 4-H), 3.26-3.41 (m, 2 H, 3-H, 4-H), 4.21 (m, 4H, 2 OCH₂), 4.44 (d, 1 H, 2-H), 7.18-8.11 (m, 6 H, aromatic H) and for *cis*-**10** at δ 1.26 (t, 6 H, 2 CH₃), 3.26-3.41 (m, 2 H, 3-H, 4-H), 3.69 (dd, 1 H, 4-H), 4.21 (m, 4 H, 2 OCH₂), 4.38 (d, 1 H, 2-H), 7.18-8.11 (m, 6 H, aromatic H). The ¹³C nmr signals were found at δ 13.9/ 14.0 (CH₃), 29.0 (C-4, *cis*), 32.9 (C-4, *trans*), 40.8/ 41.3 (C-2, C-3, *cis*), 42.5/ 44.0 (C-2, C-3, *trans*), 61.1/ 61.3/ 61.8 (OCH₂, *cis* and *trans* superimposed), 123.0/ 123.2/ 124.7/ 125.3/ 125.7/ 126.0/ 126.2/ 127.3/ 128.3/ 128.3/ 129.7/ 129.7 (aromatic CH, *cis* and *trans* superimposed), 127.8/ 128.9/ 130.1/ 130.6/ 131.5/ 131.5/ 132.3/ 132.6 (aromatic C_q, *cis* and *trans* superimposed), 170.0/ 171.5 (CO, *cis*), 170.5/ 172.6 (CO, *trans*). The FD ms spectrum showed the molecular ion M⁺ at m/z (%) 344 (100).

Anal. Calcd. for C₁₉H₂₀O₄S: C, 66.26; H, 5.85. Found: C, 66.21; H, 5.86.

Diethyl 2*H*,4*H*-Naphtho[1,2-*d*][1,3]oxathiin-2,2-dicarboxylate (**12**).

Compound **5** and mesoxalic diethyl ester (**11**) (121 mg, 0.70 mmole) formed a cycloadduct which was purified by column chromatography with light petroleum/ethyl acetate 10:1. The resulting pale yellow solid (153 mg, 69%) melted at 85° and showed ¹H nmr signals in deuteriochloroform at δ 1.16 (t, 6 H, 2 CH₃), 4.21 (q, 4 H, CH₂), 5.02 (s, 2 H, 4-H), 7.25 (d, 1 H, 5-H), 7.44-7.56 (m, 2 H, 8-H, 9-H), 7.67 (d, 1 H, 6-H), 7.79 (m, 1 H, 7-H), 8.17 (m, 1 H, 10-H) and ¹³C nmr signals at δ 13.7 (CH₃), 62.8 (OCH₂), 68.4 (C-4), 85.5 (C-2), 123.2/ 123.9/ 126.3/ 126.4/ 126.6/ 128.4 (6 aromatic CH), 127.7/ 131.2/ 132.3/ 133.0 (4 aromatic C_q), 166.2 (CO). The FD ms spectrum showed the molecular peak M⁺ at m/z (%) 346 (100).

Anal. Calcd. for C₁₈H₁₈O₅S: C, 62.41; H, 5.24. Found: C, 62.43, H, 5.27.

3-(4-Chlorophenyl)-3,4-dihydro-2-(4-methylphenyl)-2*H*-naphtho[2,1-*e*][1,3]thiazine (**14**).

Compound **5** and the Schiff base **13** (159 mg, 0.70 mmole) yielded after chromatography with light petroleum/toluene 4:1 a viscous oil (107 mg, 42%) which slowly crystalized (mp 126°). It showed ¹H nmr signals in deuteriochloroform at δ 2.36 (s, 3 H, CH₃), 4.46 (s, 2 H, 4-H), 6.31 (s, 1 H, 2-H), 7.01/ 7.19 (AA'BB', 4 H, 3-Aryl), 7.18/ 7.55 (AA'BB', 4 H, 2-Aryl), 7.20 (m, 1 H, 5-H), 7.55 (m, 2 H, 8-H, 9-H), 7.58 (m, 1 H, 6-H), 7.81 (m, 1 H, 7-H), 8.21 (m, 1 H, 10-H) and ¹³C nmr signals at δ 21.0 (CH₃), 47.9 (C-4), 67.6 (C-2), 119.4/ 123.2/ 124.6/ 125.5/ 125.9/ 126.2/ 127.9/ 128.4/ 129.1/ 129.3 (10 aromatic CH), 127.7/ 131.0/ 132.7/ 137.1/ 137.9/ 147.6 (6 aromatic C_q). The FD ms spectrum showed the molecular peak M⁺ at m/z (%) 401 (100).

Anal. Calcd. for C₂₅H₂₀ClNS: C, 74.70; H, 5.02; Cl, 8.82; N, 3.48. Found: C, 74.77; H, 5.00.

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