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Angular Benzobisthietes

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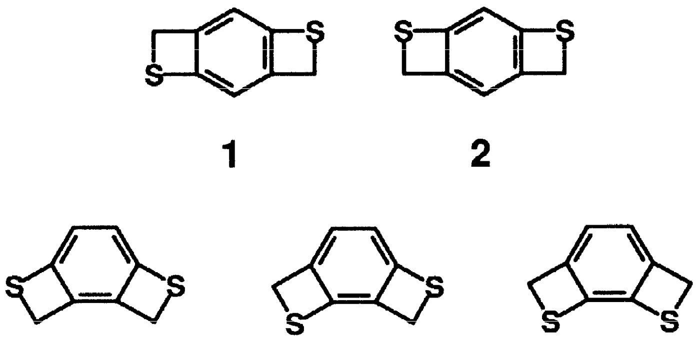
Abstract: The angular benzobisthietes **3** and **5** could be prepared by synthetic sequences in which the final step was in both cases a twofold dehydration of the corresponding bis(hydroxymethyl)dimercaptobenzenes **10** and **14**, respectively. Flash vacuum pyrolysis conditions were used for the generation and isolation of **3** and **5** which are highly reactive bisdiene systems. Cycloaddition reactions with the dienophiles **15** and **18a,b** led to the adducts **16**, **17**, and **19a,b**.

Keywords: Cyclisation; Rearrangements; Pyrolysis; Sulfur heterocycles

2*H*,5*H*-Benzo[1,2-*b*:4,5-*b'*]bisthiete (**1**) proved to be a very versatile reagent for the generation of polycyclic sulfur containing compounds[1] and moreover for linear molecular ribbons.[2] It represents a twofold diene system since gentle heating or irradiation leads to the consecutive opening of the two 4-membered rings. In principle there are five isomeric benzobisthiete structures **1** – **5**. Due to our interest in bent molecular ribbons[2,3] and cyclacenes[2,4], we studied now the generation of the angular isomers **3** and **5**.

Scheme 1



1 **2**

3 **4** **5**

The synthesis of 2*H*,3*H*-benzo[1,2-*b*:4,3-*b'*]bisthiete (**3**) was started with the 3,6-dihydroxyphthalate **6** which reacted with *N,N*-dimethylthiocarbamoyl chloride (**7**) in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO) to yield the twofold *O*-ester **8**. The isomeric twofold *S*-ester **9** was obtained by a Newman-Kwart rearrangement.[5-8] Reduction of

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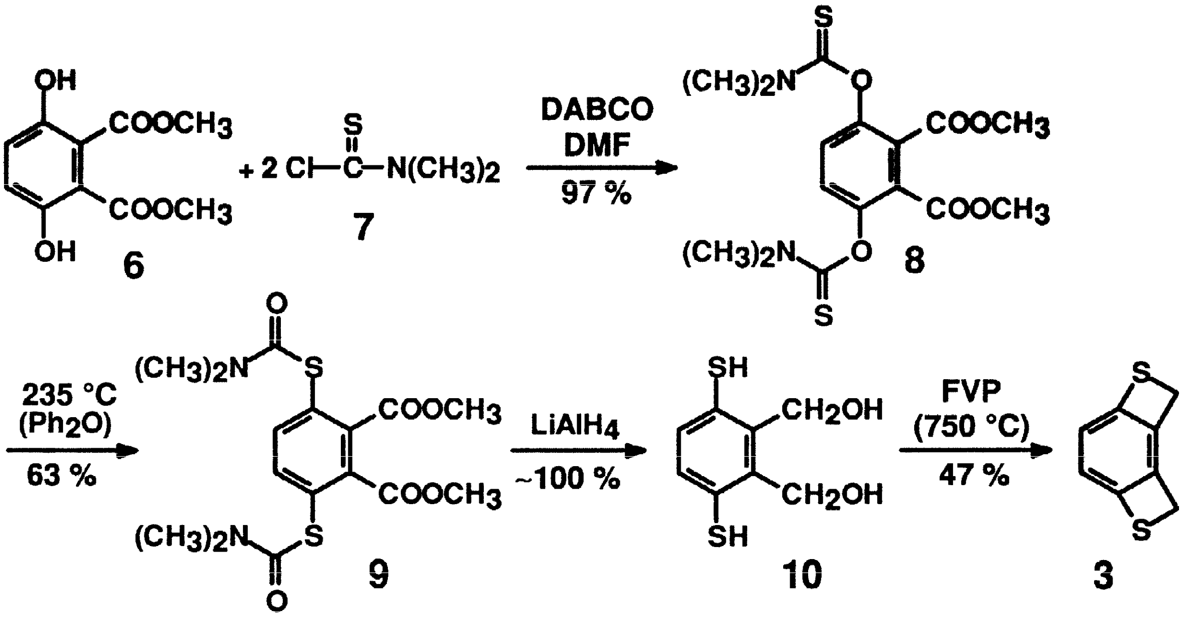
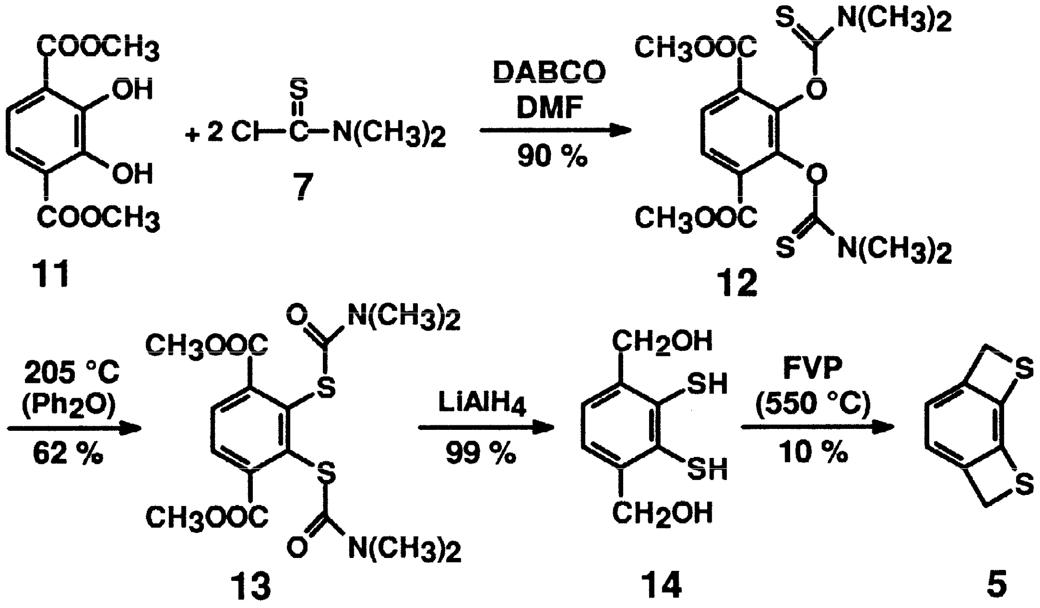
all four functional groups with $LiAlH_4$ yielded quantitatively compound **10** which is the precursor for **3**. The stepwise twofold dehydration **10** → **3** could be achieved under flash vacuum pyrolysis conditions ($1.5 \cdot 10^{-5}$ Torr, 750 °C).

Scheme 2



Starting with the 2,3-dihydroxyterephthalate **11**, a related procedure yielded 1*H*,4*H*-benzo[2,1-*b*:3,4-*b'*]bisthiete (**5**). Compared to **10** → **3** the flash pyrolysis **14** → **5** should be performed at lower temperatures ($1.5 \cdot 10^{-5}$ Torr, 550 °C). Although the flash pyrolyses are relatively clean and uniform processes, the yields of **3** and **5** are moderate, because the compound **10** and **14** tend to selfcondensation reactions, before they reach the gas phase.

Scheme 3



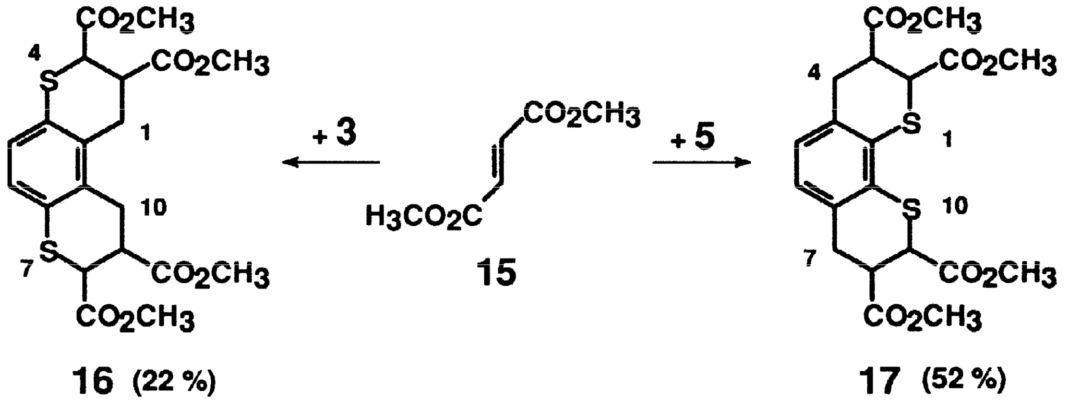
The benzobisthietes **3** and **5** were isolated in the trap (cooled by liquid nitrogen) as solid compounds which start to decompose above 90 °C. Table 1 summarizes the ^{1}H and ^{13}C NMR data in comparison to benzobisthiete **1**.

Table 1. ^{1}H and ^{13}C NMR Data of the benzobisthietes **1**, **3** and **5** (δ values measured in $CDCl_3$)

Compound	^{1}H NMR		^{13}C NMR			
	CH_2 (s, 4 H)	CH (s, 2 H)	CH_2	CH	C_q	
1	4.22	6.57	36.1	116.6	138.6	137.0
3	4.16	6.87	34.7	121.5	137.9	133.3
5	4.27	6.59	37.8	119.1	139.8	133.1

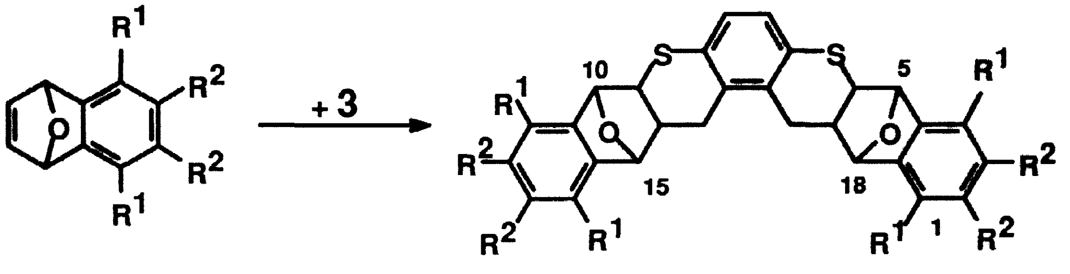
The general ability of **3** and **5** to form ring enlargement products by Diels-Alder reactions was investigated first with dimethyl fumarate (**15**). In competition to oligomerisation processes of **3** and **5** the bisadducts **16**[9] and **17**[10] were formed in boiling toluene. The consecutive [8π + 2π] cycloaddition reactions of the opened thiete rings furnish stereoselectively thiopyran rings with *trans* standing ester groups.

Scheme 4



The suitability for generating band-shaped systems was tested in two model reactions. The cycloaddition of bisthiete **3** and two molecules **18a,b** yielded the polycyclic adducts **19a,b.**[11-13] The tetrabromo compound was used because it can be transformed to a 1,4-epoxy-1,4-dihydroarene; thus, a stepwise extension of the band-shaped structure seems to be promising. According to the far distance of the reactive sites the oily cycloaddition products **16**, **17** and **19a,b** were obtained in diastereomeric ratios of 1:1 (doubled ^{1}H NMR signals).

Scheme 5



18a,b

19a (R^1 = H, R^2 = OC_6H_{13}) 48 %

19b (R^1 = C_6H_{13}, R^2 = Br) 23 %

Acknowledgments

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References and Notes

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9. Tetramethyl 1,10-dihydrobenzo[1,2-*b*:4,3-*b'*]bisthiopyran-2,3,8,9-tetracarboxylate (**16**): ^{1}H NMR ($CDCl_3$) : δ = 7.01, s, 2 H/ 6,98, s, 2 H (5-H, 6-H), 4.31, d, 2 H/ 4.28, d, 2 H (3-H, 8-H), 3.75, s, 6 H/ 3.74, s, 6 H/ 3.73, s, 6 H/ 3.72, s, 6 H (OCH_3), 3.32, m, 2 H/ 3.32, m, 2 H (2-H, 9-H), 3.21/ 2.90 (m, 8 H, 1-H, 10-H); FD MS: *m/z* = 454 (100 %, M^+).
10. Tetramethyl 4,7-dihydrobenzo[2,1-*b*:3,4-*b'*]bisthiopyran-2,3,8,9-tetracarboxylate (**17**): ^{1}H NMR ($CDCl_3$) : δ = 6.89, s, 2 H/ 6.89, s, 2 H (5-H, 6-H), 4.37, d, 2 H/ 4.35, d, 2 H (2-H, 9-H), 3.75, s, 6 H/ 3.74, s, 6 H/ 3.72, s, 6 H/ 3.72, s, 6 H (OCH_3), 3.35 – 3.06/ m, 8 H/ 2.93 – 2.80, m, 4 H (3-H, 4-H, 7-H, 8-H); FD MS: *m/z* = 454 (100 %, M^+).
11. 2,3,12,13-Tetrakis(hexyloxy)-5,5a,9a,10,15,15a,16,17,17a,18-decahydro-5,18:10,15-diepoxy-6,9-dithiaheptaphene (**19a**): ^{1}H NMR ($CDCl_3$): δ = 7.12 (s, 2 H, 7-H, 8-H), 6.87/ 6.84 (2 s, 4 H, 1-H, 4-H, 11-H, 14-H), 5.16/ 5.13 (2 s, 4 H, 5-H, 10-H, 15-H, 18-H), 3.93 (m, 8 H, OCH_2), 3.40/ 2.82 (m, 4 H, 16-H, 17-H), 3.22 (d, 2 H, 5a-H, 9a-H), 2.18 (m, 2 H, 15a-H, 17a-H), 1.76 (m, 8 H, β-CH_2), 1.44 – 1.28 (m, 24 H, CH_2), 0.88 (m, 12 H, CH_3); the doubling of the signals proves the diastereomeric ratio of 1:1. FD MS: *m/z* = 855 (100 %, M^+).
12. 2,3,12,13-Tetrabromo-1,4,11,14-tetrahexyl-5,5a,9a,10,15,15a,16,17,17a,18-decahydro-5,18:10,15-diepoxy-6,9-dithiaheptaphene (**19b**): ^{1}H NMR ($CDCl_3$): δ = 7.17 (s, 2 H, 7-H, 8-H), 5.25/ 5.23 (2 s, 4 H, 5-H, 10-H, 15-H, 18-H), 3.39/ 2.91 – 2.70 (m, 4 H, 16-H, 17-H), 3.26 (d, 2 H, 5a-H, 9a-H), 2.91 – 2.70 (m, 8 H, α-CH_2), 2.23 (m, 2 H, 15a-H, 17a-H), 1.62 – 1.31 (m, 32 H, CH_2), 0.92 (m, 12 H, CH_3). The doubling of the signals proves the diastereomeric ratio.
13. The pure diastereomers of **19a** and **19b** can be obtained by column chromatography (silica gel, petrol ether (b.p. 40 – 70 °C)/ ethyl acetate 15:1 and 50:1, respectively.