Preparation of Partially Hydrogenated 4,6-Dimethyldibenzothiophenes

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Dedicated to Professor *Giambattista Consiglio* on the occasion of his 65th birthday

The synthesis of three key intermediates of the hydrogenation pathway in the hydrodesulfurization of 4,6-dimethyldibenzothiophene (4,6-DM-DBT; **1**) is described. The hydrogenated derivatives 1,2,3,4-tetrahydro-4,6-dimethyldibenzothiophene (=4,6-dimethyl-1,2,3,4-tetrahydrodibenzothiophene; 4,6-DM-TH-DBT; **2**), 1,2,3,4,4a,9b-hexahydro-4,6-dimethyldibenzothiophene (=4,6-dimethyl-1,2,3,4,4a,9b-hexahydrodibenzothiophene; 4,6-DM-HH-DBT; **3**), and dodecahydro-4,6-dimethyldibenzothiophene (=4,6-dimethylperhydrodibenzothiophene; 4,6-DM-PH-DBT; **4**) were prepared by direct hydrogenation of **1**. The reactions were carried out in continuous and batch reactors by using metal sulfide as well as noble-metal catalysts. The influence of the reaction conditions on the formation of the products and the distribution of their stereoisomers was studied in detail. The isomers of the main products were isolated and characterized by NMR, GC/MS/MS, and X-ray crystal-structure diffractometry.

Introduction. – Polyaromatic sulfur compounds and their substituted derivatives have received a lot of attention because they are used as model compounds in hydrodesulfurization (HDS) studies [1–3]. In particular, derivatives of dibenzothiophene with the alkyl substituents in the 4- and 6-positions at the aromatic ring, adjacent to the S-atom, are the most-refractory compounds in the HDS process [4–8]. Environmental regulations decreased the maximum-acceptable amount of sulfur in gasoline and diesel fuel to 50 ppm in many parts of the world in 2005, and this limit may be reduced to 10 ppm by the end of the decade. To achieve such a low level of sulfur, deep HDS technology must be implemented. This comprises not only the development of new HDS catalysts, but also the investigation of the HDS reaction mechanism.

Extensive research has shown that the HDS of 4,6-dimethyldibenzothiophene (4,6-DM-DBT; **1**) occurs by two reaction pathways (*Fig. 1*) [4–12]. In the so-called direct desulfurization (DDS) pathway, the C–S bonds of the reactant molecule are broken by hydrogenolysis, which leads to the formation of 3,3′-dimethylbiphenyl (3,3′-DM-BP). In the hydrogenation (HYD) pathway, the reactant molecule is first hydrogenated to partially and totally hydrogenated intermediates, the C–S bonds of which are then broken in the next step to form the HDS products: 3,3′-dimethylcyclohexylbenzene (=1-methyl-3-(3-methylcyclohexyl)benzene; 3,3′-DM-CHB), and 3,3′-dimethylbicyclohexyl (3,3′-DM-BCH). The hydrogenation of the desulfurized products 3,3′-DM-BP and 3,3′-DM-CHB does not occur under the same reaction conditions, *i.e.*, in the presence of S-containing compounds. Therefore, the HDS products can only form

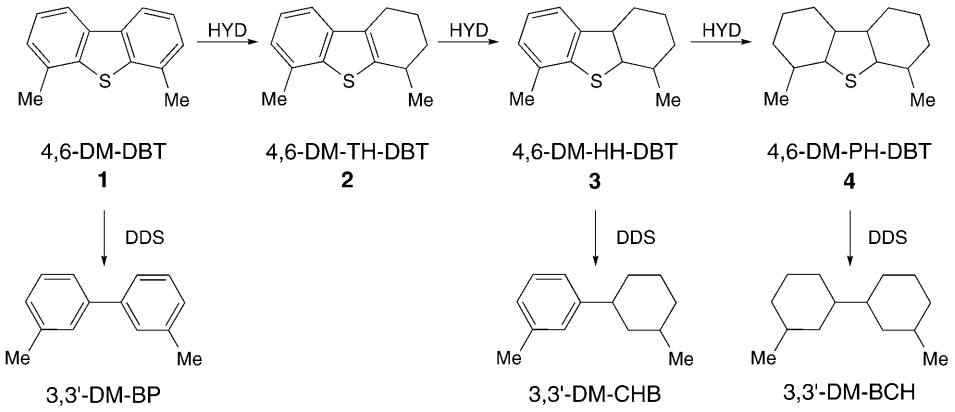

Fig. 1. *Reaction pathways of 4,6-dimethyldibenzothiophene* (**1**) *hydrodesulfurization*

from the partially or fully hydrogenated dibenzothiophenes. To investigate the reaction mechanism of the hydrodesulfurization of **1** and give a detailed description of its kinetics, the behavior of the reaction intermediates should be studied as well.

We describe here the synthesis of three key intermediates of the hydrogenation pathway of the HDS of **1**: 1,2,3,4-tetrahydro-4,6-dimethyldibenzothiophene (=4,6-dimethyl-1,2,3,4-tetrahydrodibenzothiophene; 4,6-DM-TH-DBT; **2**), 1,2,3,4,4a,9b-hexahydro-4,6-dimethyldibenzothiophene (=4,6-dimethyl-1,2,3,4,4a,9b-hexahydrodibenzothiophene; 4,6-DM-HH-DBT; **3**), and dodecahydro-4,6-dimethyldibenzothiophene (=4,6-dimethylperhydrodibenzothiophene; 4,6-DM-PH-DBT; **4**). Despite the importance of these compounds, they have not been described in the literature and, thus, we report here their preparation and properties.

There are several methodologies for the synthesis of (partially) hydrogenated derivatives of 4,6-dimethyldibenzothiophene (**1**). One is based on cyclization reactions, which result in the formation of the thiophene ring. These cyclizations are more or less variations of the *Tilak* annulation, which has been studied by several groups [13–16]. Molecules such as 1,2,3,4-tetrahydrodibenzothiophene and 1,2,3,4-tetrahydro-4-methyldibenzothiophene have been prepared by this method [13][14][16]. This type of cyclization generally provides only the tetrahydro derivatives of dibenzothiophene. Hexahydrodibenzothiophene can be prepared by reduction of the C(4a)=C(9b) bond of tetrahydrodibenzothiophene by using a Pd/C catalyst and AcOH as the solvent when the thio moiety is oxidized to a sulfone group [16]. The main drawback of this method is the intricate preparation of 2-halogeno-3-methylcyclohexanone, which is required as the starting material for the cyclization reaction and the synthesis of **2**. Another methodology is the direct reduction of **1**. Since we had access to this costly starting material, by optimizing of the preparation method described by *Kuehn-Caubère et al.* [17], we decided to investigate different methods of the direct reduction of **1**. The catalytic hydrogenation, by means of different types of catalysts and different types of reaction setups (continuous and batch), was studied in detail.

Results and Discussion. – The said procedure of *Kuehn-Caubère et al.* [17] involves the dilithiation of dibenzothiophene with an excess of BuLi at elevated temperature. The reaction is not easy since the lithiation must be carried out at high temperature, and the dilithiated intermediate must be trapped quickly with MeI to minimize by-product formation. Therefore, we added the dilithiated intermediate to the pre-cooled solution of MeI, and not *vice versa*. After the workup and crystallization, a good yield (45%) of almost pure 4,6-DM-DBT (**1**; >98%) was obtained, and its structure was confirmed by NMR and X-ray analyses.

Hydrodesulfurization studies of **1** showed that **2** is the main intermediate in the hydrogenation pathway. *Fig. 2* shows the reaction profile and the product selectivities in the HDS of **1** over sulfided Mo/γ-Al_2O_3 catalyst at 340°. The conversion reached only 26% at a space time of 5 g·min/mol, demonstrating very low activity of the molybdenum catalyst. At the same time, the product-selectivity plot clearly shows that the main reaction intermediate is 4,6-DM-TH-DBT (**2**) and that the selectivity to **2** reaches 62% at the space time $\tau = 1$ g·min/mol (*Fig. 2*). The selectivity to **2** was also measured over sulfided NiMo/γ-Al_2O_3, sulfided CoMo/γ-Al_2O_3, and metallic PtPd/γ-Al_2O_3 catalysts, but in all cases, the selectivity was lower than with sulfided Mo/γ-Al_2O_3. The reaction conditions were, therefore, optimized with a sulfided Mo/γ-Al_2O_3 catalyst (see *Table 1* for results). The reactions were carried out at two different temperatures, at two different H_2S pressures, and at various flows. The conversion of **1** was kept low because the selectivity to **2** decreased with increasing conversion (*Fig. 2*). On the other hand, the low conversion decreased the production rate, made product separation more difficult, and increased the consumption of costly reactants, especially H_2S. Therefore, the optimum conversion had to be found by varying the temperature, H_2S pressure, and flow.

Increasing the temperature from 310 to 320° increased the conversion substantially and slightly decreased the selectivity to hydrogenation products. A lower H_2S pressure hardly influenced the conversion and selectivity. A lower flow rate (higher space time) was beneficial not only for the conversion of **1**, but also for a lower H_2S consumption. *Table 2* shows the final optimized reaction conditions used to prepare **2**. The reaction was run continuously for 10 d with a conversion of *ca.* 25%. The crude product contained *ca.* 19% hydrogenation products, 14% of which represented the desired **2**. The crude product was collected every other day, and unreacted **1** was separated, purified by crystallization, and recycled back to the reaction feed. The rest of the product was adsorbed on silica gel and separated by column chromatography (petroleum ether). Products were eluted in the following order: HDS products 3,3′-DM-BP, 3,3′-DM-CHB, and 3,3′-DM-BCH: R_f 0.38–0.32; **2**: R_f 0.35; **1**: R_f 0.32–0.30; **3**: R_f 0.30–0.25; **4**: R_f 0.25–0.15. The isolated 4,6-DM-TH-DBT (**2**) was further purified by vacuum distillation, and a product of 95% purity was obtained. The main impurities were two isomers with the C=C bond shifted to the positions C(1),C(9b) and C(4),C(4a) (*i.e.*, the 2,3,4,4a-tetrahydro- and 1,2,3,9b-tetrahydro-4,6-dimethyldibenzothiophene, resp.; *cf. Fig. 3* for locants).

The fractions containing 4,6-DM-HH-DBT (**3**) were analyzed separately. They consisted of three main isomers, **3a**–**c**, in the percent ratio 53:19:28 (**3a**/**3b**/**3c**). The molecule **3** contains three stereogenic centers, *i.e.*, C(4), C(4a), and C(9b). The H-atoms at these centers can have the *cis* or *trans* configuration relative to each other, leading to

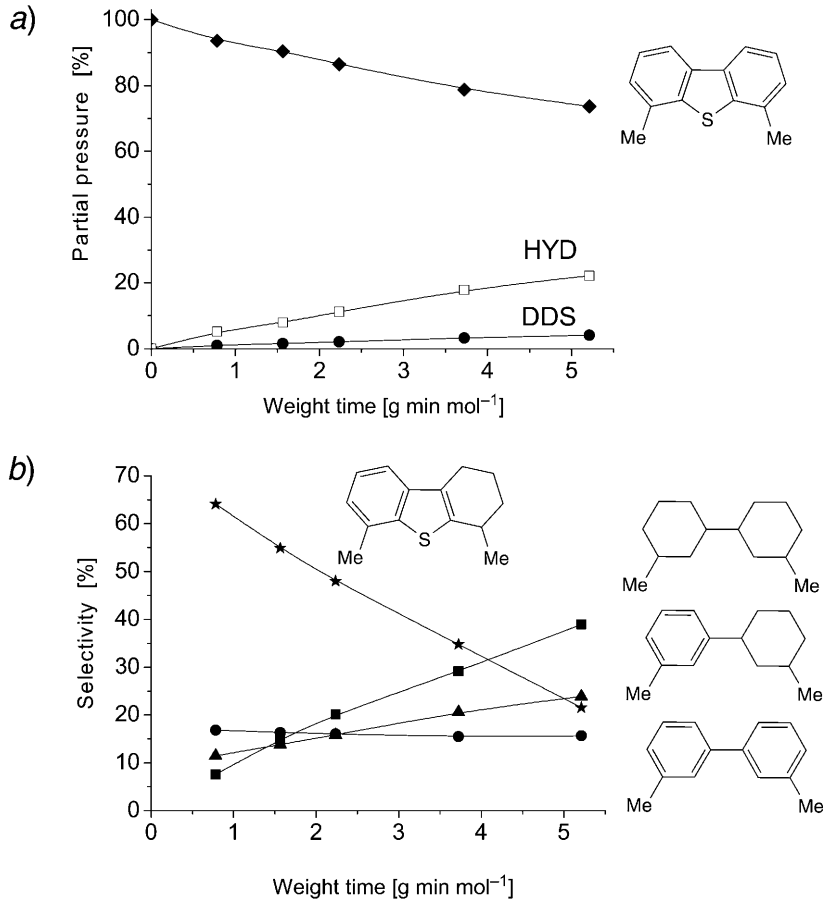

Fig. 2. a) *Reaction profiles and* b) *product selectivities in the HDS of* **1** *over sulfided Mo/γ-*Al_2O_3 *at 340°* (◆ = 4,6-DM-DBT (**1**); ★ = 4,6-DM-TH-DBT (**2**); ■ = 3,3′-DM-BCH; ▲ = 3,3′-DM-CHB; ● = 3, 3′-DM-BP)

four different diastereoisomers. Moreover, each diastereoisomer has its antipode and, thus, **3** can occur in eight different forms, *i.e.*, in four pairs of enantiomers (*Fig. 3*). The diastereoisomers of **3** obtained as by-products during the preparation of 4,6-DM-TH-DBT (**2**) were partially separated by additional column chromatography and then recrystallized from EtOH to obtain pure single diastereoisomers. They were characterized by several independent methods: NMR, MS/MS experiments, and X-ray single-crystal diffractometry. The NMR experiments differentiated the diastereoisomers by different coupling constants between H–C(4) and H–C(4a), and H–C(4) and H–C(9b) (*Table 3*). The diastereoisomer **3a** displayed one large coupling constant between H–C(4) and H–C(4a), and a small coupling constant between H–C(4a) and H–C(9), suggesting the 4,4a-*trans*;4a,9b-*cis* configuration. The diastereoisomer **3b** showed two large coupling constants, suggesting the 4,4a-*trans*;4a,9b-*trans* configuration, and the diastereoisomer **3c** showed two small, almost equal, coupling constants, suggesting

Table 1. *Optimization of the Reaction Conditions for the Production of* **2** *over Mo/γ-Al_2O_3* (various temperatures, various flows, 35 kPa H_2S)

Temperature [°]	Flow [ml/min]	Conversion [%]	*HYD*[a]) [%]	Selectivity[b]) [%]	*SEL-TH*[c]) [%]
310	0.4	6.0	5.4	92	50
310	0.3	6.5	5.9	91	62
310	0.2	10.9	9.5	87	68
320	0.4	7.4	6.6	89	57
320	0.3	10.3	9.1	88	70
320[d])	0.3	9.7	8.4	86	77
320[d])	0.2	24.5	19.1	78	71

[a]) Concentration of all sulfur-containing hydrogenated products: *HYD* = % TH + % HH + % PH). [b]) Selectivity to hydrogenated products: *SEL* = % HYD/% conversion · 100. [c]) Selectivity to 4,6-DM-TH-DBT (**2**): *SEL-TH* = % TH/% HYD · 100. [d]) 20 kPa H_2S.

Table 2. *Optimized Reaction Conditions for the Production of* **2** *from* **1**

Reaction conditions	Product composition	Production rate of **2**
Catalyst: 40 mg sulfided Mo/γ-Al_2O_3 Substrate: **1** (45 mg/ml) Solvent: toluene Temperature: 320° H_2S Pressure: 20 kPa Total pressure: 5 MPa	conversion: 24.6% selectivity: 78% hydrogenation: 19.2% (13.7% (**2**), 4.9% (**3**), 0.6% (**4**)) HDS: 5.4%	flow 0.225 ml/min, 83 mg/hour ~2 g/d continuous production for 10 d

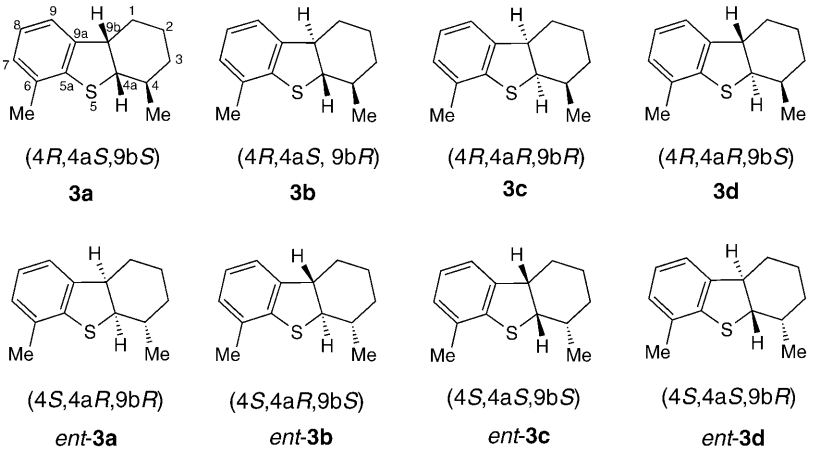

Fig. 3. *Structures of all possible stereoisomers of* **3**

the 4,4a-*cis*;4a,9b-*cis* configuration. The fourth diastereoisomer **3d** was found only in trace amounts in the reaction products, too little to be isolated for characterization. It must have the remaining 4,4a-*cis*;4a,9b-*trans* configuration. The NMR results were

confirmed by the crystal structures of the diastereoisomers **3a** (*Fig. 4*) and **3c** (*Fig. 5*). The crystal structure of isomer **3b** could not be determined, even though the quality of the crystals was good, the measured unit cell reasonable, and the found space group *P*2(1)2(1)2(1) normal. The disordered structure appeared to be so complicated that only some of the superimposed fragments of the molecule could be detected. All refinements turned out to be unstable, and the determination of an appropriate single molecule failed. The crystal structures of the diastereoisomers **3a** and **3c** confirmed the configurations found by NMR and also established that the saturated ring of **3** has the chair conformation and that the Me group attached to C(4) is in an equatorial position in both cases.

A method, that can also be applied for the differentiation of diastereoisomers is energetic resolution of the diastereoisomers by comparing their stability during electron-impact (EI) ionization with their energy content [18]. The main advantage of

Table 3. *Relative Configurations of the 4,6-DM-HH-DBT Diastereoisomers* **3a**–**d**

	J(4,4a)	*J*(4a,9b)	Configuration at		Energy [kcal/mol][a])	Bond length [Å][a])	
			C(4),C(4a)	C(4a),C(9b)		C(4a)–S	C(5a)–S
3a	10.5	6.2	*trans*	*cis*	21.07	1.91	1.84
3b	13.0	10.8	*trans*	*trans*	22.32	1.90	1.83
3c	4.7	4.7	*cis*	*cis*	21.16	1.91	1.83
3d	–	–	*cis*	*trans*	24.41	1.90	1.84

[a]) Calculated with the Hyperchem 5.0 software by using the MM+ force field.

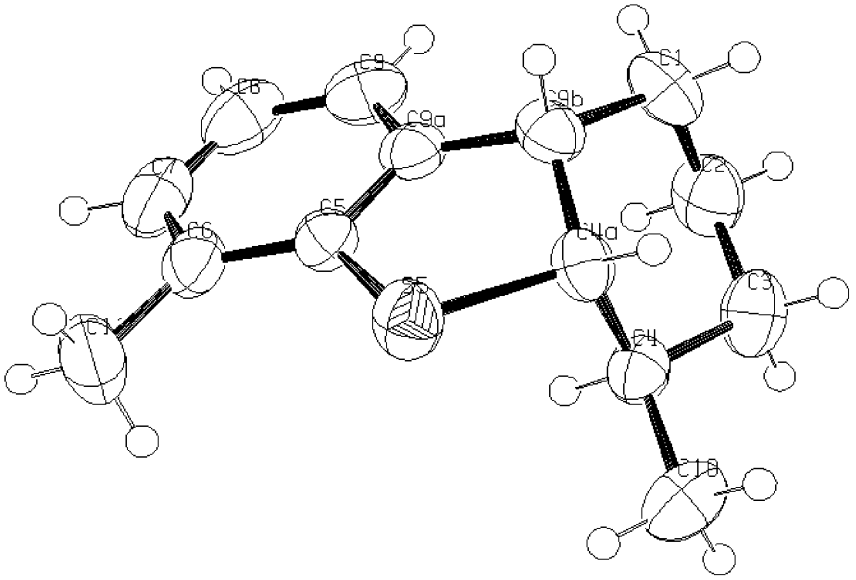

Fig. 4. *X-Ray crystal structure of* rel-*(4*R*,4a*S*,9b*S*)-1,2,3,4,4a,9b-hexahydro-4,6-dimethyldibenzothiophene* (**3a**)

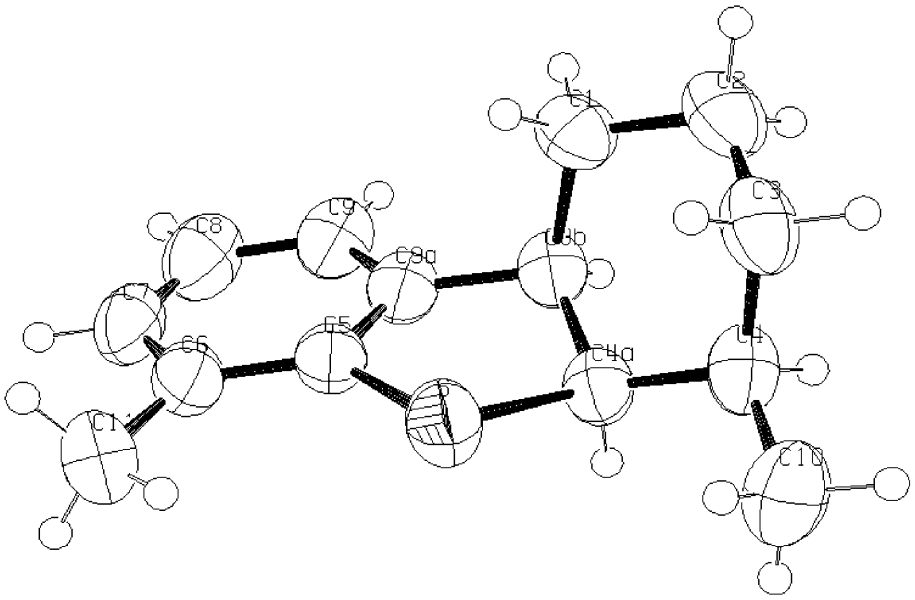

Fig. 5. *X-Ray crystal structure of* rel-*(4*R,*4a*R,*9b*R)-*1,2,3,4,4a,9b-hexahydro-4,6-dimethyldibenzothiophene* (**3c**)

this method is the direct coupling of the mass detector, which is used for energetic resolution, with chromatographic separation (*e.g.*, GC/MS/MS or HPLC/MS/MS). Thus, the separation of the diastereoisomers is unnecessary, and mixtures can be analyzed directly. The method for the differentiation of the 4,6-DM-HH-DBT diastereoisomers **3a**–**d** was optimized by varying the EI ionization and mass-detector (ion trap) parameters (temperature, amount of helium, collision-induced dissociation (CID) excitation time). The diastereoisomers were distinguished by comparing the abundance of the appropriate parent and daughter ions produced in the course of the CID experiments differing in collision energy. The MS/MS results showed that the excitation energy of the diastereoisomers increase in the order **3d** < **3b** < **3c** < **3a**. These results were compared with the energy contents of the diastereoisomers, which characterize the stability of the diastereoisomers (*Table 3*). The energy contents were obtained from molecular-mechanics calculations (MM+) with the Hyperchem 5.0 software. The order of the calculated total energies of the diastereoisomers corresponded well with that of the observed excitation energies. The molecular structures obtained from the theoretical calculations (*Fig. 6*) were also in good agreement with the crystal structures (*Figs. 4* and *5*). The calculations confirmed the chair configuration of the unsaturated ring of **3** in all the diastereoisomers and the equatorial position of the Me group at C(4) in the diastereoisomers **3a**, **3b**, and **3c**. The diastereoisomer **3d**, which has the 4,4a-*cis*;4a,9b-*trans* configuration, has also the chair conformation, but the Me group at C(4) is in an axial position. The theoretical calculations also showed that the C(4a)–S(5) bond is significantly longer than the C(5a)–S(5) bond (*Table 3*) and, in certain cases, it almost exceeded the standard C–S bond length (1.70–1.90 Å).

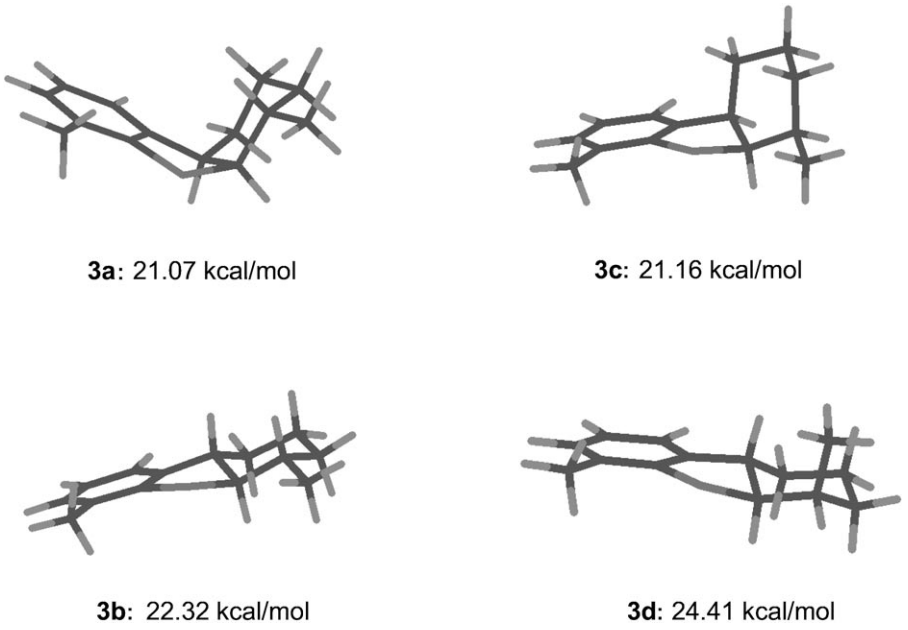

Fig. 6. *Optimized molecular structures of the 4,6-DM-HH-DBT diastereoisomers* **3a**–**d** *and their minimized energies under standard conditions*

In view of the hydrogenation pathway (*Fig. 1*), the isomers **3a** and **3c** are obviously products of the *syn*-addition of H_2 to the C(4a)=C(9b) bond of the partially hydrogenated intermediate **2**. In comparison, the isomers **3b** and **3d** have to be formed by *anti* addition of H_2 to the C(4a)=C(9b) bond or, and this is more probable, they are formed by isomerization of **3a** and **3c**. To establish that the isomerization of the diastereoisomers **3** can occur, the pure compounds **3a** and **3c** were treated separately under basic as well as under acidic conditions at high temperature (300°) for 2 h in the autoclave. The isomerization was also tested in the presence of sulfided $NiMo/Al_2O_3$ and metallic 10% Pd/C catalysts in the presence and absence of H_2. It was found that the isomerization took place only when a catalyst was present (to a greater extent over 10% Pd/C) and in the presence of H_2. Under such reaction conditions, the hydrogenation–dehydrogenation equilibrium reactions occur, and the isomers **3a** and **3c** can dehydrogenate back to **2**. The dehydrogenation takes place preferably at positions C(4a),C(9b) and C(1),C(9b) because the C=C bond remains conjugated with the unsaturated ring. While dehydrogenation and hydrogenation at position C(4a),C(9b) again gives the products with a *cis* configuration, dehydrogenation at position C(1),C(9b) results in the loss of the 4a,9b-*cis* configuration, and the 2,3,4,4a-tetrahydro-4,6-dimethyldibenzothiophene intermediate forms. Subsequent hydrogenation of this tetrahydro intermediate, formed from the **3a** and **3c** isomers, results in the other two isomers **3b** and **3d**, respectively. The formation of the intermediate with a C(1)=C(9b) bond and its fast subsequent hydrogenation to the product with the 4a,9b-*trans* configuration is analogous to the hydrogenation of naphthalene to *cis*- and *trans*-decalin (=*cis*- and *trans*-decahydro-

naphthalene). It was shown [19][20] that *cis*-decalin is formed by the hydrogenation of $\Delta^{9,10}$-octalin (=1,2,3,4,5,6,7,8-octahydronaphthalene), while *trans*-decalin is the product of $\Delta^{1,9}$-octalin (=1,2,3,4,4a,5,6,7-octahydronaphthalene).

To prepare larger amounts of **3** and **4**, the hydrogenation of **1** was studied in detail with various noble-metal catalysts. The screening experiments were carried out in a small 60-ml autoclave by using Pd, Pt, Ru, and Rh catalysts. Noble metals are easily poisoned by S-containing compounds and, therefore, large amounts of catalysts were used. The reactions were stopped when H_2 consumption stopped. The results show that the catalysts were indeed strongly deactivated, even when large amounts of catalysts were used, and that a high metal loading had a positive effect in preventing poisoning (*Table 4*). Of all the tested noble metals, 10% Pd/C was the most-active catalyst. The presence of AcOH markedly increased conversion. Therefore, further reactions were carried out with AcOH as the solvent. Other parameters, such as temperature and H_2 pressure were optimized as well. High H_2 pressure was necessary to shift the equilibrium as much as possible to the hydrogenation side. The optimal temperature had to be found because, although the conversion increased with increasing temperature, the selectivity to hydrogenated S-containing products decreased due to C–S bond cleavage and consecutive sulfur removal.

After the screening experiments, a larger autoclave (300 ml) was used to prepare larger amounts of **3** and **4**. During these experiments, the H_2 pressure was high (15 MPa) and the influence of temperature and the substrate-to-catalyst ratio on product selectivity was investigated (*Tables 5–7*). The main products at 170° were the 4,6-DM-HH-DBT diastereoisomers **3** (37% at 42% conversion; *Table 5*, *Entry 1*). The percent ratio of the hexahydro-diastereoisomers **3** was 27:10:63 (**3a**/**3b**/**3c**) (*Table 6*). At the same time, the reaction mixture contained only 1.5% of the totally saturated 4,6-DM-PH-DBT (**4**). With increasing temperature, there was an increase in the conversion as well as in the amount of **4** (up to 13%; *Table 5*, *Entry 3*). On the other hand, at 260°, the selectivity to hydrogenated products decreased because of the desulfuriza-

Table 4. *Results of the Hydrogenation of 4,6-DM-DBT* (**1**) *by Using Various Noble-Metal Catalysts*[a])

Catalyst	Temp [°]	Solvent	Conv. [%]	TH [%]	HH [%]	PH [%]	HDS [%]	*SEL*[b]) [%]
3% Pd/1% Pt/Al_2O_3	250	AcOH	8.0	3.0	4.5	0.0	0.5	94
5% Pt/Al_2O_3	250	AcOH	11.0	3.0	0.0	0.0	8.0	27
5% Ru/C	250	cyclohexane	9.0	4.0	2.5	0.0	2.5	72
5% Rh/Al_2O_3	250	AcOH	9.0	4.0	3.4	0.0	1.6	82
5% Rh/C	200	decane/HCl	45.0	11.0	17.0	1.0	16.0	64
10% Pd/C[c])	150[d])	toluene	5.0	2.0	2.0	0.0	1.0	80
10% Pd/C[c])	150[d])	toluene/AcOH	23.0	2.0	20.0	0.0	1.0	96
10% Pd/C	170[d])	AcOH	53.0	3.0	39.0	4.0	7.0	87
10% Pd/C	250	AcOH	77.0	8.0	35.0	13.0	21.0	73

[a]) Reaction conditions: 250 mg of substrate, 250 mg of catalyst, 20 ml of solvent, 13 MPa H_2. [b]) Selectivity to hydrogenated products: $SEL = (\%\ TH + \%\ HH + \%\ PH)/\%\,\text{conversion} \cdot 100$. [c]) 125 mg of catalyst. [d]) 8 MPa H_2.

tion reaction. The percent ratio of the diastereoisomers **3** also changed at higher temperature and a more equilibrated mixture of isomers was obtained: **3a**/**3b**/**3c** 32:17:50 (*Table 6*, *Entry 3*). This is in good agreement with the isomerization experiments. At lower temperatures, *syn* addition of H_2 takes place in particular and the major product is the diastereoisomer **3c**. The amount of the other diastereoisomers increased with increasing temperature due to the hydrogenation–dehydrogenation equilibrium. We also carried out an experiment in which the reaction time was ten times longer (*Table 6*, *Entry 4*). The conversion remained almost the same, but the percent ratio of the diastereoisomers shifted to 40:14:45 (**3a**/**3b**/**3c**). This result coincides well with the energy contents of the diastereoisomers as obtained from theoretical calculations. They showed that **3a** and **3c** have almost the same energy and are more stable than **3b** (*Fig. 6*). The calculated energy of the diastereoisomer **3d**, which was present in the reaction mixtures, but only in trace amounts (< 0.1%), was *ca.* 2 kcal/mol higher than that of diastereoisomer **3b**. The highest energy content and, thus, the lowest stability of isomer **3d** are probably caused by the axial position of the Me group at C(4).

The highest selectivity to 4,6-DM-PH-DBT (**4**) (33%) was obtained at 200° by using a large amount of catalyst (the substrate-to-catalyst molar ratio was decreased to 3; *Table 7*, *Entry 5*). These reaction conditions resulted in high conversion (71%) and a yield of 24% of **4** (*Table 5*). The rest of the product consisted mainly of 4,6-DM-HH-DBT isomers **3** (41%). The products of all the hydrogenation reactions were separated by double-column chromatography, and the isomers of **3** were purified by crystalliza-

Table 5. *Hydrogenation of* **1** *over 10% Pd/C under Various Reaction Conditions*[a])

Entry	Temp. [°]	Conversion [%]	TH [%]	HH [%]	PH [%]	HDS [%]	*SEL* [%][b])
1	170	42	1.7	36.9	1.5	1.9	95.5
2	210	53	3.6	40.7	6.4	2.3	95.7
3	260	61	7.5	23.5	13.0	17	72.1
4	200[c])	58	3.7	40.3	8.9	5.1	91.2
5	200[d])	71	2.6	40.9	23.7	3.8	94.6

[a]) 5 g of substrate, 5 g of catalyst, 180 ml of AcOH, 15 MPa H_2, 2 h. [b]) Selectivity to hydrogenated products: *SEL* = (% TH + % HH + % PH)/% conversion · 100. [c]) 10 g of substrate, 10 g of catalyst, 20 h. [d]) 10 g of substrate, 15 g of catalyst, 5 h.

Table 6. *Distribution of the 4,6-DM-HH-DBT Diastereoisomers* **3** *during the Hydrogenation of* **1** *over 10% Pd/C*[a])

Entry	Temp. [°]	Conversion [%]	**3a** [%]	**3b** [%]	**3c** [%]	**3d** [%]	*SEL-HH* [%][b])
1	170	42	26.6	10.3	63.1	–	87.9
2	210	53	31.0	11.3	57.7	–	76.8
3	260	61	31.5	16.6	49.8	2.1	38.5
4	200[c])	58	39.5	13.6	44.7	2.2	70.7
5	200[d])	71	35.5	5.9	58.6	–	57.6

[a]) 5 g of substrate, 5 g of catalyst, 180 ml of AcOH, 15 MPa H_2, 2 h. [b]) Selectivity to HH isomers: *SEL-HH* = % HH/% conversion · 100. [c]) 10 g of substrate, 10 g of catalyst, 20 h. [d]) 10 g of substrate, 15 g of catalyst, 5 h.

Table 7. *Distribution of the 4,6-DM-PH-DBT Diastereoisomers* **4** *during the Hydrogenation of* **1** *over 10% Pd/C*[a])

Entry	Temp. [°]	Conversion [%]	**4a** [%]	**4b** [%]	**4c** [%]	**4d** [%]	*SEL-PH* [%][b])
1	170	42	0	7	64	29	3.6
2	210	53	4	23	47	26	12.1
3	260	61	11	49	13	27	21.3
4	200[c])	58	4	34	36	26	15.6
5	200[d])	71	2	18	53	27	33.4

[a]) 5 g of substrate, 5 g of catalyst, 180 ml of AcOH, 15 MPa H_2, 2 h. [b]) Selectivity to PH isomers: *SEL-PH* = % PH/% conversion · 100. [c]) 10 g of substrate, 10 g of catalyst, 20 h. [d]) 10 g of substrate, 15 g of catalyst, 5 h.

tion. The mixture of the 4,6-DM-PH-DBT isomers **4** was further separated by column chromatography, and the isomers with the highest concentration were isolated and characterized by NMR spectroscopy.

Compound **4** contains six stereogenic centers and can contain a plane of symmetry. Therefore, the maximum number of different 4,6-DM-PH-DBT diastereoisomers is 20 (16 pairs of enantiomers and 4 *meso* forms), and not $2^5 = 32$. We observed 10 peaks with *m*/*z* 224 in our product by using GC/MS. Most of these peaks were, however, very small, meaning that the corresponding isomers were present in the reaction mixture but only in a very low concentration. We successfully separated four major isomers, **4a**–**d**, and characterized them by NMR experiments (*Table 8*). The isomers were differentiated by the interaction constants between H–C(4) and H–C(4a), H–C(4a) and H–C(9b), H–C(5a) and H–C(6), and H–C(5a) and H–C(9a). All four isomers had the same *cis* configuration between C(4a) and C(9b), and *trans* configuration between C(5a) and C(9a). The configuration between C(9a) and C(9b) could not be determined because the signals of H–C(9a) and H–C(9b) overlapped with the signals of other H-atoms of the molecule. The only case, in which the signals were well separated was for isomer **4c**. The NMR signals of its H-atoms were split by four neighboring H-atoms into complicated *multiplets*. Simulation of the NMR spectrum and comparison with the measured spectrum established the *cis* configuration between C(9a) and C(9b) in the **4c** isomer. Both isomers **4b** and **4d** possess the 5a,6-*cis*;5a,9a-*trans* configuration, which suggests that the Me group at C(6) occupies the axial position. This was confirmed by the lower chemical shifts of the Me group of the **4b** and **4d** isomers in the ^{13}C-NMR spectra (δ 12.1 and 12.3, resp.). Isomers **4a** and **4c** both have Me groups in equatorial positions.

The major isomer formed at low temperature (*Table 7*, *Entry 1*) was **4c** with 4,4a-*cis*;4a,9b-*cis*;5a,6-*trans*;5a,9a-*trans*;9a,9b-*cis* configuration (*Fig. 7*). Isomer **4c** is probably formed by consecutive isomerization and *cis* hydrogenation of **3c**, the most abundant isomer of **3** at low temperature. Molecule **3c** is not flat, as the starting molecule **1**, and the hydrogenated ring is perpendicular to the plane of benzothiophene (*Figs. 5* and *6*). During the *syn*-hydrogenation of the second benzene ring, a product with all-*cis*-configuration would be expected. In this structure, both hydrogenated rings would be oriented in the same direction, *i.e.*, perpendicular to the plane of tetrahydrothiophene. Both hydrogenated rings would be so close that they would sterically hinder

Table 8. *Relative Configurations of the 4,6-DM-PH-DBT Diastereoisomers* **4a**–**d**

	J(4,4a)	*J*(4a,9b)	*J*(5a,6)	*J*(5a,9a)	Configuration at			
					C(4),C(4a)	C(4a),C(9b)	C(5a),C(6)	C(5a)C(9a)
4a	10.8	6.6	10.5	10.5	*trans*	*cis*	*trans*	*trans*
4b	10.8	5.8	4.0	10.7	*trans*	*cis*	*cis*	*trans*
4c	4.3	4.3	10.7	9.1	*cis*	*cis*	*trans*	*trans*
4d	4.3	4.3	4.3	11.7	*cis*	*cis*	*cis*	*trans*

not only each other but also the adsorption through the S-atom. In agreement with this, the minimal energy (28.50 kcal/mol) calculated for this molecular structure was significantly higher than the energy of other 4,6-DM-PH-DBT isomers **4** (between 20 and 26 kcal/mol). Instead of the product with all-*cis* configuration, the much more stable (21.05 kcal/mol) **4c** isomer with 4,4a-*cis*;4a,9b-*cis*;5a,6-*trans*;5a,9a-*trans*;9a,9b-*cis* configuration formed (*Fig. 7*). As shown for isomer **3c**, the bond C(4a)–S is elongated to such an extent (*Table 3*) that it can be easily split, and the configuration around C(4a) can change from *cis,cis* to *trans,trans*. The *syn*-hydrogenation of the isomer with *trans,trans* configuration around C(4a) would then result in the isomer **4c**.

(4*S*,4a*S*,5a*S*,6*R*,9a*R*,9b*S*)
4c

(4*R*,4a*R*,5a*R*,6*S*,9a*S*,9b*R*)
ent-**4c**

Fig. 7. *Structure of the main isomer* **4c** *of 4,6-DM-PH-DBT*

The major isomer formed at high temperature (*Table 7*, *Entry 3*) was **4b** followed by **4d**. Both have one Me group in the axial position and the 5a,9a-*trans* configuration. The isomer **4b** may be formed by *syn* hydrogenation of isomer **3a**, which first gives 4,6-DM-PH-DBT with 4,4a-*trans*;4a,9b-*cis*;5a,6-*cis*;5a,9a-*cis*;9a,9b-*cis* configuration. Molecule **3a** is not flat and, similar to **3c**, the hydrogenated ring is perpendicular to the plane of the dihydrobenzothiophene ring. Therefore, isomers **3a** and **3c** can only adsorb from one side of the benzothiophene ring and, thus, the hydrogenation of **3a** and **3c** would always give products with 9a,9b-*cis* configuration. On the other hand, the molecular calculations showed that products with all-*cis* configuration at the tetrahydrothiophene ring, *i.e.*, H–C(4a), H–C(5a), H–C(9a), H–C(9b) on the same side, are much less stable than isomers that have at least one of the H-atoms on the opposite side. Thus, the product molecules tend to acquire this energetically more stable configuration. This can take place by dehydrogenation and subsequent hydrogenation, similar as in case of the isomerization of the 4,6-DM-HH-DBT isomers **3a**–**d**, or the hydrogenation of naphthalene to *cis*- and *trans*-decalin [19][20]. The product of *syn* hydrogenation of **3a** is 4,6-DM-PH-DBT with the 4,4a-*trans*;4a,9b-*cis*;5a,6-*cis*;5a,9a-*cis*;9a,9b-*cis*

configuration (24.04 kcal/mol). This molecule can be dehydrogenated in positions C(9),C(9a) to 1,2,3,4,4a,5a,6,7,8,9b-decahydro-4,6-dimethyldibenzothiophene, which is then hydrogenated to the more stable isomer **4b** (22.56 kcal/mol). Similarly, isomer **4d** may be a product of dehydrogenation–hydrogenation of isomer **3c**. The hydrogenated intermediate with all-*cis* configuration (28.50 kcal/mol) may isomerize by dehydrogenation and hydrogenation to the more stable isomer **4d** (24.38 kcal/mol). The last isomer isolated from the reaction mixture was the isomer **4a**. It may form by isomerization of 4,6-DM-PH-DBT with 4,4a-*trans*;4a,9b-*cis*;5a,6-*trans*;5a,9a-*cis*;9a,9b-*cis* configuration (31.08 kcal/mol). Such an intermediate could only be a product of *syn* hydrogenation of 1,2,3,4,6,7,8,9-octahydro-4,6-dimethyldibenzothiophene. However, it will readily isomerize due to its high energy to the much more stable isomer **4a** (20.64 kcal/mol).

At low temperature, the isomers **4c** and **4d** (both formed from **3c**) were the main isomers of 4,6-DM-PH-DBT (**4**) (*Table 7*, *Entry 1*). This is in good agreement with the distribution of the 4,6-DM-HH-DBT isomers **3a**–**d**, which shows that the predominant isomer under the same reaction conditions was isomer **3c** (*Table 6*, *Entry 1*). With increasing temperature, the content of isomer **4b** (formed from **3a**) increased, to the detriment of isomer **4c**. This also agrees with the distribution of the 4,6-DM-HH-DBT isomers **3**, where the content of isomer **3a** increased to the detriment of isomer **3c**.

At high temperature (*Table 7*, *Entry 3*), more-equilibrated mixtures of the 4,6-DM-PH-DBT isomers **4a**–**d** as well as of the 4,6-DM-HH-DBT isomers **3a**–**d** were produced by hydrogenation–dehydrogenation reactions on the surface of the noble-metal catalyst. The isomerization can be caused not only by fast hydrogenation–dehydrogenation reactions at higher reaction temperature, but also by splitting and reforming of the C(4a)–S(5), C(5a)–S(5), or C(9a)–C(9b) bonds of the partially hydrogenated thiophene ring.

Conclusions. – We have demonstrated that the direct reduction of 4,6-dimethyldibenzothiophene (4,6-DM-DBT; **1**) over heterogeneous catalysts can be applied to prepare partially and totally hydrogenated 4,6-dimethyldibenzothiophenes. The three key intermediates of the hydrogenation pathway of the hydrodesulfurization of **1** were prepared: 1,2,3,4-tetrahydro-4,6-dimethyldibenzothiophene (**2**), 1,2,3,4,4a,9b-hexahydro-4,6-dimethyldibenzothiophene (**3**), and perhydro-4,6-dimethyldibenzothiophene (**4**). The products were used to investigate the reaction mechanism and the kinetics of the hydrodesulfurization of **1** over metallic Pd as well as over sulfided Mo and NiMo/γ-Al_2O_3 catalysts [21][22]. It was shown that **1** reacts almost exclusively through the hydrogenation pathway and that the partially and totally hydrogenated intermediates desulfurize much easier than **1**. This is explained by the molecular changes around the S-atom upon hydrogenation. First, the planarity of **1** is removed and, thus, the steric encumbrance of the S-atom by the Me groups decreases. Second, the bond between the S- and C-atoms belonging to the hydrogenated ring elongates significantly. These results of hydrogenation provide better access to the S-atom and, thus, enhanced removal of the S-atom from the reaction intermediates.

Special attention was paid to the configuration of the products and the isolation and characterization of the main isomers formed during hydrogenation reactions. It was shown that the products of the *syn* addition of H_2 form preferentially when noble-

metal catalysts were used. The resulting *cis* isomers readily isomerized to equilibrium mixtures, especially at higher reaction temperatures, due to fast hydrogenation–dehydrogenation reactions. Nevertheless, reasonable amounts of the pure isomers of the main products, namely **2**, **3a**, **3c**, **4c**, and **4d**, were separated and purified (from 1 up to 20 grams). The further study of the HDS mechanism with single diastereoisomers at a lower reaction temperature provided more information about the nature of the active sites of the HDS catalysts.

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Experimental Part

General. Column chromatography (CC): *Fluka* silica gel *60* (0.04–0.063 mm); eluent petroleum ether (b.p. 110–140°). TLC: *Merck* TLC plates precoated with silica gel *60* F_{254}; visualization by treatment with *Mostain* soln. GC: *HP-5890-II-Plus-Agilent* instrument equipped with an *HP-1* capillary column; t_R in min. ^{1}H- and ^{13}C-NMR spectroscopy: *Bruker-DPX-300* and *Bruker-Avance-500* spectrometers; δ in ppm, J in Hz. GC/MS: *Agilent-GC-MS* (*HP 6890 MSD*) equipped with an *HP-5MS* column (30 m × 0.25 mm × 0.25 μm); in *m/z* (rel. %). MS/MS Experiments: *GC-MS/MS-Saturn-2000-Varian* instrument equipped with *CP-Sil-8-CB-Lowbleed/MS* column and an ion-trap mass detector; EI ionization, trap temp. 80°, emission current 10 μA, axial modulation voltage 2.5 V, isolation time for ion preparation 10 ms; dissociation: resonant waveform type, excitation time 2 ms. Elementary analysis: automatic analyzer *Perkin Elmer CHN 240C*.

X-Ray Diffraction Analyses. The crystal structures of isolated crystalline products were determined by X-ray single-crystal diffraction analysis by using *Oxford-Xcalibur* and *Picker-Stoe-Dif4* X-ray diffractometers. The crystallographic data were validated with the PLATON program. Crystal data and details of structure refinement of **3a** and **3c** are given in *Table 9*.

Hydrogenation Procedure. The experiments were performed in the liquid phase in a 60- or 300-ml stainless-steel autoclave (*Premex AG*) equipped with a sampling tube and a magnetic gas-inducing impeller. Several noble-metal catalysts on different supports were used in screening experiments: 10 wt-% Pd/C (*Acros*); 5 wt-% Pt/Al_2O_3, 5 wt-% Ru/C, 5 wt-% Rh/C, 5 wt-% Rh/Al_2O_3 (all *Fluka*); 3% Pd/1% Pt/Al_2O_3 (prepared by incipient wetness impregnation of γ-Al_2O_3 with a 5% aq. soln. of $Pd(NH_3)(NO_3)_2$, drying at 120°, and calcining at 500° for 4 h). The catalyst (usually 250 mg) and solvent (30 ml) were placed in the reactor, and an appropriate amount of **1** (250 mg) was added. A rather large amount of catalyst with respect to the substrate was required to obtain a reasonable reaction time because of the poisoning effect of the S-atom in the substrate molecule. The autoclave was closed, and the air was displaced first with N_2 (3×) and then with H_2 (3×). The autoclave was pressurized with H_2 to the desired value (8–13 MPa), and stirring (1000 rpm) and heating to the appropriate temp. (150–250°) were started. Samples of the reaction mixture were withdrawn during the reaction and analyzed by GC. After the hydrogenation was complete, the catalyst was filtered off and washed several times with CH_2Cl_2. The solvent was evaporated, and the final product was analyzed by GC and GC/MS.

4,6-Dimethyldibenzothiophene (**1**). To a soln. of dry hexane (200 ml) and *N*,*N*,*N*′,*N*′-tetramethylethane-1,2-diamine (TMEDA; 74.4 g, 96 ml) was added dropwise 1.6M BuLi in hexane (400 ml) at 0°. The mixture was stirred for 30 min at 0° and then 30 min at r.t. It was diluted with additional hexane (400 ml), the dibenzothiophene (39 g) was added, and the mixture was heated to 60° and stirred for 2 h. The yellow suspension was cooled to −15° and added in parts through a *Teflon* tube (6×4 mm) to a precooled soln. of MeI (91 g, 20 ml) in hexane (200 ml). The mixture was cooled during this process by a dry ice/liq. N_2/aceton mixture so that the temp. did not exceed −70°. Stirring was continued for 12 h, during which the mixture was allowed to reach r.t. The mixture was poured into a flask containing

Table 9. *Crystal Data and Details of Structure Refinement of 4,6-DM-HH-DBT Isomers* **3a** and **3c**[a])

	3a	**3c**
Formula	$C_{14}H_{18}S$	$C_{14}H_{18}S$
M_r	218.34	218.34
System	monoclinic	orthorhombic
Space group	*P2*(1)/*c*	*Pbca*
Crystal size [mm]	0.1×0.1×0.08	0.1×0.1×0.07
a [Å]	7.6530(15)	14.3771(15)
b [Å]	16.585(3)	8.8904(7)
c [Å]	10.244(2)	19.1231(19)
α [°]	90.00	90.00
β [°]	111.06	90.00
γ [°]	90.00	90.00
V [Å^3]	1213.4(5)	2444.3(4)
Z	4	8
D_x [g·cm^{-3}]	1.195	1.187
T [K]	295(2)	295(2)
μ [mm^{-1}]	2.057	0.230
F(000)	472	944
2θ Range [°]	5.33–67.07	4.18–27.59
Measured reflections	2333	16023
Unique reflections	2165	2820
Observed reflections	1830	1896
Number of variables	137	136
R_1 and wR_2 ($I>2\sigma(I)$)	0.8686; 0.1775	0.0817; 0.2060
R_1 and wR_2 (all data)	0.0782; 0.1924	0.1170; 0.2275
Goodness of fit	1.110	1.107
Final $\Delta\rho$ [eÅ^{-3}]	0.526; −0.782	0.235; −0.235

[a]) The isomers **3a** and **3c** were measured on a *Picker-Stoe-Dif4* diffractometer with Cu-K_α radiation and a *Oxford-Excalibur* diffractometer with MoK_α radiation, resp. Standard data reduction and absorption corrections were applied. Structure solution and refinement was performed with the SHELX program package. CCDC 296765 (**3a**) and CCDC 296766 (**3c**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the *Cambridge Crystallographic Data Centre via* www.ccdc.cam.ac.uk/data_request/cif.

1.5 l of ice-water and extracted with toluene (3×600 ml). The org. phase was washed with 1M HCl (1×600 ml) and H_2O (3×600 ml), dried ($MgSO_4$), and evaporated. The crude product was recrystallized from THF: 20 g (45%; >98% GC purity) of **1**. White needle-like crystals. M.p. 154° ([17]: m.p. 154°). TLC: R_f 0.32. GC (inj. 300°; det. 300°; temp. program: 200° for 2 min, heating rate 10°/min, 280° for 5 min): t_R 4.84. ^{1}H-NMR ($CDCl_3$, 300 MHz): 2.57 (*s*, Me–C(4), Me–C(6)); 7.21 (*d*, *J*=7.2, 2 H); 7.38 (*t*, *J*=7.5, 2 H); 7.98 (*d*, *J*=7.8, 2 H). ^{13}C-NMR (DEPT, $CDCl_3$, 125 MHz): 20.5 (2*q*, Me–C(4), Me–C(6)); 119.3, 124.7, 126.8 (6*d*); 132.2, 136.0, 139.3 (6*s*). EI-MS: 212 (100), 197 (15), 105 (13). Anal. calc. for $C_{14}H_{12}S$ (212.32): C 79.20, H 5.70, S 15.10; found: C 79.23, H 5.78, S 15.23. The X-ray crystal structure of **1** was identical with the structure published elsewhere [23].

1,2,3,4-Tetrahydro-4,6-dimethyldibenzothiophene (**2**). The synthesis of **2** from **1** was performed in a continuous plug-flow fix-bed reactor usually used in hydrodesulfurization experiments [24]. Two types of catalysts were used, a bimetallic 3 wt-% Pd/1 wt-% Pt/Al_2O_3 catalyst and a 8 wt-% sulfided Mo/γ-Al_2O_3 catalyst, both prepared by incipient wetness impregnation [21][25]. The reactor was loaded with 40 to 75 mg of catalyst mixed with SiC (8 g) to achieve plug-flow conditions. The molybdenum catalyst was activated prior to the reaction by *in situ* sulfidation with a mixture of 10% H_2S in H_2 (50 N ml/min) at 400°

and 1 MPa for 4 h. The molybdenum catalyst was more effective in the production of **2** than the Pd/Pt bimetallic catalyst, and the optimized reaction conditions with the molybdenum catalyst were as follow: the temp. was decreased to 320° and the total pressure increased to 5 MPa; the liquid reactants were fed to the reactor. The gas-phase feed consisted of 130 kPa toluene (as solvent), 2.5 kPa **1** (almost the limit of solubility; 45 mg/ml), 20 kPa H_2S, and *ca.* 4.85 MPa H_2. The reaction was carried out at a space time of $\tau = 4.9$ g·min/mol. Under these conditions, the product mixture consisted of 69% of **1**, 18% of **2**, 6.5% of **3**, 0.5% of **4**, and 6% of desulfurized products. After partial evaporation of the solvent, unreacted **1** was recovered by repeated crystallization in toluene. The formed crystals of **1** were filtered, and the remaining mother liquor was added to commercial silica gel and evaporated to dryness. The reaction products were separated by CC (SiO_2, petroleum ether). The fractions containing **2** were further purified by vacuum distillation (b.p. 105–109°/26 Pa): **2** of 95% purity. Colorless liquid, which turned slightly yellow with time. The main impurities (5%) were two isomers with the C=C bond shifted to the positions C(1),C(9b) and C(4),C(4a), *i.e.*, 2,3,4,4a-tetrahydro- and 1,2,3,9b-tetrahydro-4,6-dimethyldibenzothiophene, resp.

Data of **2**: TLC: R_f 0.35. GC (inj. 300°; det. 300°; temp. program: 200° for 2 min, heating rate 10°/min, 280° for 5 min): t_R 4.33. ^{1}H-NMR ($CDCl_3$, 500 MHz): 1.35 (*d*, *J* = 6.9, Me–C(4)); 1.48–1.54 (*m*, 1 H–C(3)); 1.72–1.81 (*m*, 1 H–C(2)), 1.97–2.07 (*m*, 1 H–C(2), 1 H–C(3)); 2.50 (*s*, Me–C(6)); 2.61–2.67 (*m*, 1 H–C(1)); 2.72–2.77 (*m*, 1 H–C(1)); 3.01–3.05 (*m*, H–C(4)); 7.04 (*d*, *J* = 7.4, H–C(7)); 7.24 (*t*, *J* = 7.5, H–C(8)); 7.38 (*d*, *J* = 7.8, H–C(9)). ^{13}C-NMR (DEPT, $CDCl_3$, 125 MHz): 20.3 (*q*, *Me*–C(6)); 21.5 (*t*, C(2)); 22.9 (*q*, *Me*–C(4)); 24.0 (*t*, C(1)); 31.7 (*d*, C(4)); 32.8 (*t*, C(3)); 118.4 (*d*, C(9)); 123.9 (*d*, C(8)); 124.2 (*d*, C(7)); 130.0 (*s*, C(9b)); 131.7 (*s*, C(6)); 138.5 (*s*, C(5a)); 139.6 (*s*, C(9a)); 143.0 (*s*, C(4a)). EI-MS: 216 (78), 201 (100), 188 (36), 186 (17), 171 (17). Anal. calc. for $C_{14}H_{16}S$ (216.35): C 77.72, H 7.45, S 14.82; found: C 77.81, H 7.42, S 14.87.

1,2,3,4,4a,9b-Hexahydro-4,6-dimethyldibenzothiophene (**3**). Compound **3** was prepared by hydrogenation of **1** at high H_2 pressure in a 300-ml stainless-steel autoclave. The autoclave was loaded with 10 wt-% Pd/C catalyst (10 g), **1** (10 g), and AcOH (180 ml; as solvent, crucial for a high conversion). The reaction was carried out at 200° and 15 MPa H_2 for 5 h. The hydrogenation product consisted of 47% of **1**, 4% of **2**, 42% of **3**, 4% of **4**, and 3% of desulfurized products. After cooling the autoclave to r.t., the catalyst was filtered off. Since a large amount of product remained adsorbed on the catalyst, the catalyst was refluxed in $CHCl_3$ for 1 h and filtered again. Both filtrates were then evaporated separately, and unreacted **1** was purified by recrystallization from toluene. The mother liquors were evaporated together with commercial silica gel, and the reaction products were separated twice by CC as described for **2**. There were three different isomers of **3** in the reaction mixture in the following proportions: 28% of **3a**, 9% of **3b**, and 63% of **3c**. The isomers were partly separated by CC and further purified by crystallization from EtOH to obtain pure white crystalline compounds for full characterization (^{1}H- and ^{13}C-NMR, MS/MS experiments, X-ray single-crystal diffraction analysis). For crystallographic data and details of structural determination of isomers **3a** and **3c**, see above, *Table 9*.

*rel-(4*R*,4a*S*,9b*S*)-1,2,3,4,4a,9b-Hexahydro-4,6-dimethyldibenzothiophene* (**3a**). TLC: R_f 0.27. GC (inj. 300°; det. 300°; temp. program: 200° for 2 min, heating rate of 10°/min, 280° for 5 min): t_R 3.50. M.p. 87–89°. ^{1}H-NMR (C_6D_6, 500 MHz): 0.65–0.72 (*m*, *J* = 3.2, 12.7, 1 H–C(3)); 0.90 (*d*, *J* = 6.5, Me–C(4)); 1.15–1.23 (*m*, *J* = 3.2, 12.7, 1 H–C(2), H–C(4)); 1.28–1.45 (*m*, 1 H–C(2), 1 H–C(3), 1 H–C(1)); 2.06 (*m*, *J* = 2.4, 3.3, 14.2, 1 H–C(1)); 2.22 (*s*, Me–C(6)); 2.78 (*dd*, *J* = 6.2, 10.5, H–C(4a)); 3.30 (br. *s*, H–C(9b)); 6.80 (*d*, *J* = 7.4, H–C(9)); 6.85 (*d*, *J* = 7.4, H–C(7)); 6.97 (*t*, *J* = 7.4, H–C(8)). ^{13}C-NMR (DEPT, C_6D_6, 125 MHz): 20.6 (*q*, *Me*–C(6)); 21.4 (*q*, *Me*–C(4)); 21.6 (*t*, C(2)); 26.2 (*t*, C(1)); 33.7 (*t*, C(3)); 35.2 (*d*, C(4)); 48.8 (*d*, C(9b)); 59.5 (*d*, C(4a)); 120.9 (*d*, C(9)); 124.6 (*d*, C(8)); 128.1 (*d*, C(7)); 132.6 (*s*, C(6)); 141.0 (*s*, C(9a)); 142.3 (*s*, C(5a)). EI-MS: 218 (100), 175 (37), 161 (70), 149 (36), 128 (8), 115 (10). Anal. calc. for $C_{14}H_{18}S$ (218.36): C 77.01, H 8.31, S 14.68; found: C 77.10, H 8.27, S 14.71.

rel-*(4*R*,4a*S*,9b*R*)-1,2,3,4,4a,9b-Hexahydro-4,6-dimethyldibenzothiophene* (**3b**): TLC: R_f 0.26. GC (inj. 300°; det. 300°; temp. program: 200° for 2 min, heating rate 10°/min, 280° for 5 min): t_R 3.70. ^{1}H-NMR (C_6D_6, 500 MHz): 0.67–0.82 (*ddd*, *J* = 4.1, 11.7, 13.0, 1 H–C(3)); 0.95 (*d*, *J* = 6.5, Me–C(4)); 1.03–1.18 (*m*, 1 H–C(1), 1 H–C(2)); 1.47–1.50 (*m*, *J* = 3.5, 13.4, 1 H–C(3)); 1.54–1.57 (*m*, 1 H–C(2)); 1.70–1.78 (*m*, H–C(4)); 1.98 (*dd*, *J* = 3.3, 11.0, 1 H–C(1)); 2.25 (*s*, Me–C(6)); 2.73 (*ddd*, *J* = 3.1, 10.8, H–C(9b)); 2.89 (*dd*, *J* = 10.8, 13.0, H–C(4a)); 6.81 (*d*, *J* = 7.3, H–C(9)); 6.87 (*d*, *J* = 7.3, H–C(7)); 6.95 (*t*, *J* = 7.4, H–C(8)). ^{13}C-NMR (DEPT, C_6D_6, 125 MHz): 20.7 (*q*, *Me*–C(6)); 22.0 (*q*,

Me–C(4)); 26.0 (*t*, C(2)); 28.4 (*t*, C(1)); 35.3 (*t*, C(3)); 37.5 (*d*, C(4)); 54.4 (*d*, C(9b)); 66.0 (*d*, C(4a)); 119.9 (*d*, C(9)); 124.6 (*d*, C(8)); 128.4 (*d*, C(7)); 132.4 (*s*, C(6)); 141.9 (*s*, C(9a)); 143.7 (*s*, C(5a)). EI-MS: 218 (100), 175 (28), 161 (70), 147 (19), 128 (10), 115 (10). Anal. calc. for $C_{14}H_{18}S$ (218.36): C 77.01, H 8.31, S 14.68; found: C 76.90, H 8.39, S 14.61.

rel-*(4*R*,4a*R*,9b*R*)-1,2,3,4,4a,9b-Hexahydro-4,6-dimethyldibenzothiophene* (**3c**): TLC: R_f 0.25. GC (inj. 300°; det. 300°; temp. program: 200° for 2 min, heating rate 10°/min, 280° for 5 min): t_R 3.56. M.p. 72–75°. ^{1}H-NMR (C_6D_6, 500 MHz): 1.00 (*d*, *J* = 6.7, Me–C(4)); 1.02–1.07 (*m*, 1 H–C(2)); 1.28–1.31 (*m*, 1 H–C(3)); 1.37–1.41 (*m*, 1 H–C(1)); 1.44–1.60 (*m*, 1 H–C(3), 1 H–C(1), 1 H–C(2), H–C(4)); 2.22 (*s*, Me–C(6)); 2.70 (*ddd*, *J* = 5.3, 5.8, 11.3, H–C(9b)); 3.96 (*t*, *J* = 4.9, H–C(4a)); 6.83 (*d*, *J* = 7.4, H–C(7)); 6.87 (*d*, *J* = 6.7, H–C(9)); 6.91 (*t*, *J* = 7.3, H–C(8)). ^{13}C-NMR (DEPT, C_6D_6, 125 MHz): 20.8 (*q*, *Me*–C(6)); 22.3 (*q*, *Me*–C(4)); 25.1 (*t*, C(2)); 28.6 (*t*, C(1)); 28.9 (*t*, C(3)); 33.6 (*d*, C(4)); 48.7 (*d*, C(9b)); 59.8 (*d*, C(4a)); 121.3 (*d*, C(9)); 124.6 (*d*, C(8)); 128.2 (*d*, C(7)); 132.8 (*s*, C(6)); 140.1 (*s*, C(9a)); 146.1 (*s*, C(5a)). EI-MS: 218 (100), 175 (37), 161 (65), 149 (34), 128 (7), 115 (8). Anal. calc. for $C_{14}H_{18}S$ (218.36): C 77.01, H 8.31, S 14.68; found: C 77.07, H 8.29, S 14.65.

Dodecahydro-4,6-dimethyldibenzothiophene (**4**). As described for **3**, but with a lower S/C ratio (15 g of 10% Pd/C catalyst were used for reduction of 10 g of **1**). Under the same conditions (200°, 15 MPa H_2, 5 h), the hydrogenation product contained 29% of **1**, 3% of **2**, 41% of **3**, 23% of **4**, and 4% of desulfurized products. Compound **4** has 20 different diastereoisomers. Under our reaction conditions, we observed ten of them, but only 4 reached a concentration higher than 0.5%. These were separated by CC as colorless liquids and were characterized by MS, ^{1}H- and ^{13}C-NMR.

4,4a-trans*;4a,9b*-cis*;5a,6*-trans*;5a,9a*-trans-*Dodecahydro-4,6-dimethyldibenzothiophene* (**4a**): TLC: R_f 0.22. GC (inj. 300°; det. 300°; temp. program: 200° for 2 min, heating rate 10°/min, 280° for 5 min): t_R 3.11. ^{1}H-NMR ($CDCl_3$, 500 MHz): 0.89 (*d*, Me); 0.96 (*d*, Me); 1.05–2.00 (*m*, 16 H); 2.48 (*dd*, *J*(5a,6) = 10.5, *J*(5a,9a) = 10.5, H–C(5a)); 2.80 (*dd*, *J*(4a,4) = 10.8, *J*(4a,9b) = 6.6, H–C(4a)). ^{13}C-NMR (DEPT, $CDCl_3$, 125 MHz): 21.0, 21.4 (2*q*); 21.9, 25.9, 26.1, 29.3, 35.0, 35.5 (6*t*); 40.0, 40.05, 47.2, 47.4, 54.6, 60.4 (6*d*). EI-MS: 224 (100), 190 (58), 167 (28), 153 (55), 108 (33), 95 (51). Anal. calc. for $C_{14}H_{24}S$ (224.41): C 74.93, H 10.78, S 14.28; found: C 74.98, H 10.69, S 14.31.

4,4a-trans*;4a,9b*-cis*;5a,6-cis;5a,9a*-trans-*Dodecahydro-4,6-dimethyldibenzothiophene* (**4b**): TLC: R_f 0.19. GC (inj. 300°; det. 300°; temp. program: 200° for 2 min, heating rate 10°/min, 280° for 5 min): t_R 3.33. ^{1}H-NMR ($CDCl_3$, 500 MHz): 0.89 (*d*, Me); 1.02 (*d*, Me); 1.14–2.17 (*m*, 16 H); 2.73 (*dd*, *J*(4a,4) = 10.8, *J*(4a,9b) = 5.7, H–C(4a)); 3.10 (*dd*, *J*(5a,6) = 4.0, *J*(5a,9a) = 10.6, H–C(5a)). ^{13}C-NMR (DEPT, $CDCl_3$, 125 MHz): 12.1, 20.0 (2*q*); 21.0, 21.4, 25.5, 26.7, 30.5, 32.5 (6*t*); 35.0, 39.0, 39.6, 47.3, 54.7, 57.2 (6*d*). EI-MS: 224 (100), 190 (44), 167 (30), 153 (65), 108 (30), 95 (65). Anal. calc. for $C_{14}H_{24}S$ (224.41): C 74.93, H 10.78, S 14.28; found: C 75.0, H 10.71, S 14.34.

4,4a-cis*;4a,9b*-cis*;5a,6*-trans*;5a,9a*-trans*;9a,9b*-cis-*Dodecahydro-4,6-dimethyldibenzothiophene* (**4c**): TLC: R_f 0.17. GC (inj. 300°; det. 300°; temp. program: 200° for 2 min, heating rate 10°/min, 280° for 5 min): t_R 3.50. ^{1}H-NMR ($CDCl_3$, 500 MHz): 0.90 (*d*, *J* = 6.2, Me); 0.95 (*d*, *J* = 6.8, Me); 1.02–1.18 (*m*, 2 H); 1.32–1.45 (*m*, 3 H); 1.51–1.64 (*m*, 5 H); 1.72–1.78 (*m*, 2 H); 1.85–1.93 (*m*, 2 H); 2.04 (*dddd*, *J*(1,9b) = 5.7, 12.0, *J*(4a,9b) = 4.3, *J*(9a,9b) = 5.5, H–C(9b)); 2.29 (*dddd*, *J*(5a,9a) = 9.1, *J*(9a,9b) = 5.5, *J*(9,9a) = 2.2, 7.2, H–C(9a)); 2.87 (*dd*, *J*(5a,6) = 10.7, *J*(5a,9a) = 9.1, H–C(5a)); 3.64 (*dd*, *J*(4a,4) = 4.3, *J*(4a,9b) = 4.3, H–C(4a)). ^{13}C-NMR (DEPT, $CDCl_3$, 125 MHz): 22.0, 22.7 (2*q*); 23.5, 25.1, 25.7, 26.1, 28.2, 33.2 (6*t*); 33.9, 40.1, 44.5, 49.4, 53.0, 55.8 (6*d*). EI-MS: 224 (100), 190 (8), 181 (23), 167 (36), 153 (25), 95 (23). Anal. calc. for $C_{14}H_{24}S$ (224.41): C 74.93, H 10.78, S 14.28; found: C 74.95, H 10.80, S 14.25.

4,4a-cis*;4a,9b*-cis*;5a,6*-cis*;5a,9a*-trans-*Dodecahydro-4,6-dimethyldibenzothiophene* (**4d**): TLC: R_f 0.22. GC (inj. 300°; det. 300°; temp. program: 200° for 2 min, heating rate 10°/min, 280° for 5 min): t_R 3.57. ^{1}H-NMR ($CDCl_3$, 500 MHz): 0.94 (*d*, Me); 1.06 (*d*, Me); 1.15–2.05 (*m*, 16 H); 3.27 (*dd*, *J*(5a,6) = 4.2, *J*(5a,9a) = 11.7, H–C(5a)); 3.68 (*dd*, *J*(4a,4) = 4.3, *J*(4a,9b) = 4.3, H–C(4a)). ^{13}C-NMR (DEPT, $CDCl_3$, 125 MHz): 12.3, 20.4 (2*q*); 21.8, 21.9, 25.1, 28.0, 28.4, 31.0 (6*t*); 32.6, 34.3, 45.8, 46.1, 52.0, 55.7 (6*d*). EI-MS: 224 (100), 181 (20), 167 (31), 153 (37), 95 (36). Anal. calc. for $C_{14}H_{24}S$ (224.41): C 74.93, H 10.78, S 14.28; found: C 75.01, H 10.83, S 14.34.

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