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An Efficient Synthesis of Pure 4,6-Dimethyldibenzothiophene

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Abstract : The synthesis of substituted dibenzothiophenes in the 4 and/or 6 positions has been optimized and pure 4,6-dimethyldibenzothiophene has been prepared by a new selective method; X-ray analysis of this compound is described.

Substituted dibenzothiophenes have in the past years attracted the attention of several scientific groups. These products, and especially 4-methyl- and 4,6-dimethyldibenzothiophene (4-MDBT and 4,6-DMDBT) are the sulfur containing compounds in diesel fuel that remain the ones most difficult to desulfurize.[1-3] Due to more stringent environmental regulations to protect urban areas (Clean Air Act in the USA) and new legislations in Europe, the sulfur level in diesel fuel has to be limited to less than 0.05 wt.-%. Actually, present refinery diesel hydrodesulfurization processes can only lead to such a low level under severe pressure and temperature conditions that shorten catalyst life. Therefore the elucidation of the hydrodesulfurization mechanism of these refractory molecules could provide new ideas for the design of more effective or selective catalysts.

However, the study of the transformation of mono- or polysubstituted dibenzothiophenes is seriously slowed down because of difficulties encountered during the synthesis of these compounds. Moreover, because of their low accessibility and although these compounds or their derivatives are supposed to have an odor similar to that of roses,[4] no practical application of such products was developed until now. An access to dibenzothiophene (DBT) **(1)** substituted in the 4 position has been described over fifty years ago by Gilman and Jacoby.[5] This reaction involves treatment of dibenzothiophene with *n*-butyllithium to form 4-lithio-dibenzothiophene, which reacts with electrophiles leading to the formation of 4-substituted dibenzothiophenes (Fig.1).

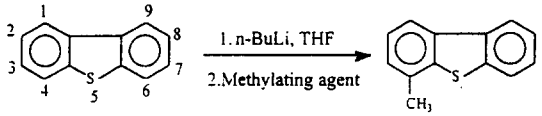

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Fig.1. Synthesis of 4-methyldibenzothiophene

Up to now, mainly this method has been used for the preparation of various 4-substituted dibenzothiophenes.[6-9] We have modified this synthesis to obtain 4-methyldibenzothiophene as a model molecule for hydrodesulfurization studies.[3]
Our results are summarized in Table 1 (entries 1 to 3).

Table 1. Synthetic Conditions for the Metallation and Methylation of Dibenzothiophene.

Entry	Substrate	Base	Eq.[a]	DBT[b]	4-MDBT[b]	4,6-DMDBT[b]	4-EDBT[b]
1	DBT	n-BuLi	1.5	10	86	-	-
2	DBT	s-BuLi	4	19	81	-	-
3	DBT	MeLi	4	75	25	-	-
4	DBT	n-BuLi	4	21	60	12	-
5	DBT	n-BuLi	6	17	55	17	-
6	4-MDBT	n-BuLi	2	8	22	7	63

[a] molar ratio Base/Substrate (and Methyl iodide/Substrate)
[b] GC yield

Even with an excess of base, dibenzothiophene is never completely transformed. The best conversion is obtained with *n*-butyllithium as a base and reaches 86% (GC yield) (Table 1, entry 1). The unconverted dibenzothiophene is hardly to be removed, even after several recrystallizations or silica gel chromatography columns : we thus obtained 4-methyldibenzothiophene with 91% purity. Boberg *et al.*[10] have published the results of the separation of the corresponding sulfoxides; however the purity of their alkylated DBT is not reported.

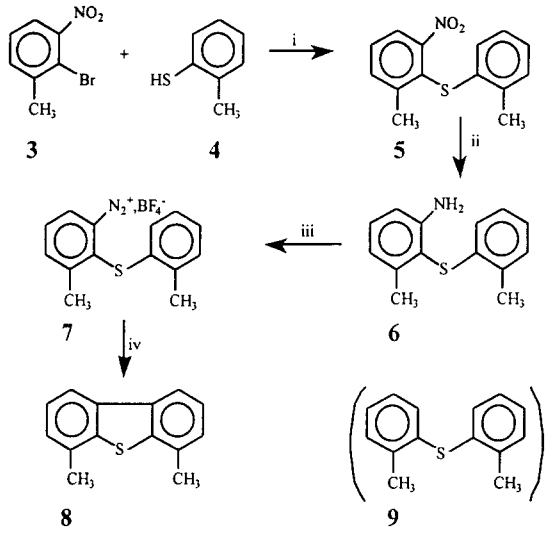
The use of the same method with a great excess of base and electrophile could theoretically lead to 4,6-disubstituted dibenzothiophenes, because of the similarity between the two positions. However, all studies on the synthesis of 4,6-dimethyldibenzothiophene have shown that the above mentioned method led to a mixture of monomethyldibenzothiophene as the major product and 4,6-dimethyldibenzothiophene in a low yield.[8-11] We have obtained comparable results (Table 1, entries 4-5) under similar conditions. The introduction of the two methyl groups by a successive two-step synthesis (i.e. lithiation and methylation of isolated 4-methyldibenzothiophene) has been extensively studied by Katritzky and Perumal[8], but this procedure affords 4-ethyldibenzothiophene (4-EDBT) as the major product, the lithiation of the methyl group being preferred to the transformation of the 6 position of 4-methyldibenzothiophene. The same observation has been made recently by Boberg *et al.*[10] (see also Table 1, entry 6). We have checked by MNDO calculations that the electronic repartition on the molecule is in agreement with these experimental results. Moreover, the separation

of the mixture of mono- and dialkyldibenzothiophenes thus obtained is not easily feasible; pure 4,6-dimethyldibenzothiophene can not be prepared by this method at a preparative scale.

In order to prevent the difficulties due to this preparation, we have turned out our efforts to a synthesis of pure 4,6-dimethyldibenzothiophene by the construction of the system from two aromatic rings and/or by their internal cyclization. The synthesis of dibenzothiophene and 4-methyldibenzothiophene according to this new pathway has already been explored by different groups. Zeller *et al.*[12] have indeed prepared dibenzothiophene by photocyclization of diphenyl sulfide in 54% yield. The cyclization of diphenyl sulfide, via the reduction of its sulfoxide by sodium amide, was also performed by Schönberg.[13] Although the claimed yield was not attractive (25% for the last step), we have checked this procedure with o,o'-ditolyl sulfide, however, without success until now. Catalytic cyclizations of several diphenyl products were also tested by Åkermark[14] but, in the case of diphenyl sulfide, the expected product, dibenzothiophene, was not obtained. Dibenzothiophene has been prepared by Pd-catalyzed intramolecular cyclization of 2-cyclohexenyl 2-iodophenyl sulfide (Heck-type reaction) and aromatization with 25% global yield.[15] A step-by-step construction of the aromatic system has been described by Black and Cadogan;[16,17] they have prepared dibenzothiophene and 4-methyldibenzothiophene by flash vacuum pyrolysis of appropriate benzoates. Gilman and Jacoby[5] have synthesized 4-methyldibenzothiophene by ring closure of 3-methyl-2,2'-dihydroxybiphenyl with phosphorus pentasulfide. The preparation of the corresponding 3,3'-dimethyl-2,2'-dihydroxybiphenyl to obtain the disubstituted 4,6-dimethyldibenzothiophene however remains difficult and not exploitable at a gram scale.[18] Campaigne *et al.*[6] have found another method to synthesize pure 4-methyldibenzothiophene, free from unreacted dibenzothiophene. It involves first the reaction between o-thiocresol and 2-chloro cyclohexanone followed by cyclization of the keto sulfide thus obtained to 1,2,3,4-tetrahydro-6-methyldibenzothiophene. After aromatization with selenium, 4-methyldibenzothiophene is obtained in 56% yield.[7] This smart procedure, however, is again applicable with difficulty to the production of 4,6-dimethyldibenzothiophene because of the difficult access to 2-halogeno-3-methylcyclohexanone, and the fastidious purification at the end of the synthesis.

We have chosen to develop a new method, applicable at a large scale, that gives a direct access to pure 4,6-dimethyldibenzothiophene.

This route also involves the coupling of two aromatic rings first by a nucleophilic substitution, then by a Pschorr-type reaction, as illustrated in Fig. 2. Thus a nucleophilic substitution occuring in N-methyl-2-pyrrolidinone between 2-bromo-3-nitrotoluene **(3)** and o-thiocresol **(4)** analogous to Campbell,[19] leads to the desired substituted diphenyl sulfide **5** with 85% yield. The nitro function is then reduced at hydrogen atmospheric pressure with palladium on charcoal in methanol[20] and gives the analogous amino compound **6** with a good yield after recrystallization (90%). This primary aromatic amine is then transformed in its diazonium salt by the addition of sodium nitrite in sulfuric acid.[21] This last compound is isolated as its stable fluoroborate salt **7**. Finally, the intramolecular cyclization is run with copper as catalyst in dimethyl sulfoxide at room temperature and leads to the formation of pure 4,6-dimethyldibenzothiophene **8** as white needles after recrystallization in cyclohexane/isopropanol mixture.



i: KOH, NMP, 170°C, 85%; ii: Pd/C, MeOH, H_2, 1 atm, RT, 90%;
iii: H_2SO_4,$NaNO_2$, $NaBF_4$, 0°C; iv: Cu, DMSO, RT, 25%.

Fig. 2. Target synthesis towards 4,6-dimethyldibenzothiophene

This last cyclization has been described for the preparation of dibenzothiophene, using *t*-butyl thionitrate at 160°C;[4,22] these drastic conditions are, however, not easily applicable. We have then first tested the reaction in acetone, as described for other molecules,[21] but this solvent provided the reduced molecule di-o-tolyl sulfide **9** as an important by-product. The use of DMSO allows a decrease in the amount of **9**; the by-products, oligomers or polymers, are easily removed by a filtration column. After recrystallization, 4,6-dimethyldibenzothiophene is obtained with 19% overall yield, with a sufficient purity (> 99%) to allow an X-ray crystal structure determination (Fig. 3).

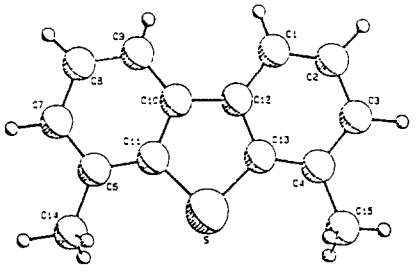


Fig. 3. X-ray crystal stucture of 4,6-dimethyldibenzothiophene **(8)**

The X-ray crystal structure presents several differences with that obtained using MM2 and MNDO calculations. Particularly, the solid state internal angle that defines the molecule around the sulfur atom are noticeably larger (C_{13}-S-C_{11}, 92.1°) than the calculated one by our different methods of calculations

(respectively 87.1° and 88.6°). The importance of this internal deformation on the stability and/or the low reactivity of 4,6-DMDBT toward desulfurization has to be questioned.

The synthetic method, in four steps, does not require special equipment, high temperature or pressure, is easily reproducible and permits to obtain rapidly several grams of 4,6-dimethyldibenzothiophene with a high purity (> 99%). The easy access to 4,6-dimethyldibenzothiophene described in this article permits the study of its desulfurization pathway and then may lead to the conception of new more efficient catalysts. The study of the isomerization of such a sterically hindered molecule into other more easy to desulfurize dimethyldibenzothiophene isomers is at present in progress in our laboratories. Moreover, the X-ray structure described here is of special interest for theoretical chemists working on understanding the difference of reactivities of similar molecules towards desulfurization.

EXPERIMENTAL

Melting points were determined on a Heizbank system Kofler type WME (± 1°C). The ^{1}H NMR and ^{13}C NMR spectra were obtained on a Bruker AC 200 (200 and 50 MHz respectively), chemical shifts were reported in ppm. The IR spectra were obtained on a Perkin-Elmer 1720-X. Elementary analyses were performed by the Service Central d'Analyses, CNRS, Solaize, France.

4-Methyldibenzothiophene (2)

Dibenzothiophene (30 g, 163 mmoles) was dissolved in THF (240 ml) under argon atmosphere. 152 ml of a 1.6 M solution of *n*-butyllithium in hexanes (245 mmoles) were added dropwise to the reaction mixture which was then refluxed for 1½ h. After cooling at 0°C, 15.25 ml of methyl iodide (245 mmoles) were added slowly and the mixture was let one night at room temperature.

It was then put into a flask containing 800 ml of ice-water. The product was extracted with ethyl acetate (2 x 250 ml), the organic phase was washed, dried over magnesium sulfate and the solvent was removed. The brown oil obtained (35 g) was purified on a silica column using cyclohexane as the eluent to give 29 g of white powder which was recrystallized from methanol (180 ml); 20.5 g of 4-MDBT (63% yield, 91% GC purity) as white plates were thus obtained, mp 64°C; ^{1}H NMR (deuteriochloroform): δ 2.6 (s, 3H, CH_3), 7.2-7.3 (d, 1H, H-Ar, J = 7 Hz), 7.4-7.5 (m, 3H, H-Ar), 7.8-7.9 (m, 1H, H-Ar), 8.0-8.1 (d, 1H, H-Ar, J = 7 Hz), 8.1-8.2 (m, 1H, H-Ar).

2-Methylphenyl 2-methyl-6-nitrophenyl sulfide (5)

A suspension of 5.8 g of potassium hydroxide (102 mmoles) in 67 ml of N-methyl-2-pyrrolidinone was vigorously stirred at room temperature. O-thiocresol (10.9 ml, 93 mmoles) was added dropwise to the reaction mixture. After heating 1½ h at 170°C, the reaction mixture was cooled at 120°C and 2-bromo-3-nitrotoluene (20 g, 93 mmoles) was added in several portions.

The mixture was again heated 1½ h at 170°C, cooled, and put into a flask containing 550 ml of ice water. The product was extracted with dichloromethane (4 x 250 ml), dried over magnesium sulfate and evaporated. The residue (68 g) was purified on a silica column using cyclohexane/ethyl acetate (97/3) as the eluent to give 21 g of **5** as a yellow powder (85% yield), mp 88°C; ^{1}H NMR (deuteriochloroform): δ 2.3 and 2.4 (s, 2x3H, 2xCH_3), 6.7 (dd, 1H, H-3', $J_{3',4'}$ = 7 Hz, $J_{3',5'}$ = 2 Hz), 7.0-7.5 (m, 5H, H-Ar-4'-5'-6'-3-4), 7.6 (dd, 1H, H-5, J_{5-4}

= 7 Hz, J_{5-3} = 2 Hz); ^{13}C NMR (deuteriochloroform): δ 20.19 (C_2-$\underline{C}H_3$), 21.29 ($C_{2'}$-$\underline{C}H_3$), 121.34 (C_5), 125.87 (C_1), 126.29, 126.75, 127.50, 129.25 and 130.37 (C_4, $C_{3'}$, $C_{4'}$, $C_{5'}$ and $C_{6'}$), 130.50 ($C_{1'}$), 133.69 (C_3), 134.58 and 136.47 (C_2 and $C_{2'}$), 145.32 (C_6); IR (KBr): Ar-NO_2 1376 and 1534 cm^{-1}.

2-Methylphenyl 2-methyl-6-aminophenyl sulfide (6)

Product **5** (21 g, 81 mmoles) was hydrogenated at hydrogen atmospheric pressure in methanol (200 ml), the catalyst being Pd/C, 10% (4.2 g catalyst, 4 mmoles of Pd). After one day stirring at room temperature, the mixture was filtered over celite and the solvent was then evaporated. The obtained product was recrystallized in isopropanol (130 ml) to give 16.7 g of **6** as a brown powder (90% yield), mp 138°C; ^{1}H NMR (deuteriochloroform): δ 2.3 and 2.4 (s, 2x3H, 2xCH_3), 4.0 (s, 2H, NH_2), 6.2-7.5 (m,7H, H-Ar); ^{13}C NMR (deuteriochloroform): δ 19.94 and 21.48 (C_2-$\underline{C}H_3$ and $C_{2'}$-$\underline{C}H_3$), 112.88 (C_5), 113.33 (C_1), 120.15 (C_3), 123.71, 124.64, 126.56, 130.07 and 130.45 (C_4, $C_{3'}$, $C_{4'}$, $C_{5'}$ and $C_{6'}$), 134.87, 135.54 and 144.81 (C_2, $C_{1'}$ and $C_{2'}$), 149.83 (C_6); IR (KBr): Ar-NH_2 1600, 3374 and 3474 cm^{-1}.

Anal. Calcd. for $C_{14}H_{15}NS$: C, 73.33; H, 6.60; N, 6.11; S, 13.96. Found: C, 73.05; H, 6.57; N, 6.09; S, 14.38.

2-Methylphenyl 2-methyl-6-diazophenyl sulfide fluoroborate (7)

Product **6** (12.3 g, 54 mmoles) was heated in 175 ml H_2SO_4, 30% in order to obtain a fine dispersion. After cooling at 0°C, a solution of sodium nitrite 40% (8.45 ml, 73 mmoles) in 23 ml of water was added dropwise. Then, a solution of sodium fluoroborate (11.6 g, 106 mmoles) in 23 ml of water was added to the mixture which was, after 5 minutes stirring, filtered and dried off. The product thus obtained, **7**, was used in the next reaction without any further purification.

4,6-Dimethyldibenzothiophene (8)

The obtained diazonium salt **7** (17.6 g) was added in several portions to a suspension of copper (10.5 g, 165 mmoles) in DMSO (880 ml). After 2 hours stirring at room temperature, the mixture was filtered and 2 liters of ice-water were added, giving an exothermicity of 30°C. The brown product in suspension was filtered, dried and then purified on a silica column using cyclohexane as the eluent. A white powder (4.3 g) was obtained. Being recrystallized in 80 ml of isopropanol and 25 ml of cyclohexane, 3 g of **8** as white needles (26% yield) were obtained, mp 152°C; ^{1}H NMR (deuteriochloroform): δ 2.6 (s, 2x3H, 2xCH_3), 7.2 (d, 2x1H, H-3, J_{3-2} = 7 Hz), 7.4 (t, 2x1H, H-2 and H-8, J_{2-3} = 7 Hz), 8.0 (d, 2x1H, H-1, J_{1-2} = 7 Hz); ^{13}C NMR (deuteriochloroform): δ 20.56 (C_4-$\underline{C}H_3$ and C_6-$\underline{C}H_3$), 119.33 (C_1 and C_9), 124.76 (C_2 and C_8), 126.89 (C_3 and C_7), 132.26, 136.09 and 139.37 (C_4, C_6, C_{10}, C_{11}, C_{12} and C_{13}).

Anal. Calcd. for $C_{14}H_{12}S$: C, 79.2; H, 5.7; S, 15.1. Found: C, 79.36; H, 5.61; S, 15.16.

X-ray structure analysis of (8)

Single crystals suitable for X-ray structure analysis were prepared from a dilute solution of 4,6-dimethyldibenzothiophene (**8**) in isopropanol / cyclohexane 3,2 / 1.

Crystal Data : $C_{14}H_{12}S$, M_W = 212.3, monoclinic, space group $P2_1/c$, a = 7.590(1). b = 11.909(2), c = 14.885(3) Å, β = 126.18(1)°, V = 1086.1(4) Å^3, Z = 4, D_c = 1.299 g.cm^{-3}, λ(CuKα) = 1.5424 Å, μ(CuKα) = 7.0 cm^{-1}.

The diffraction data were collected from a single crystal of 0.05 x 0.35 x 0.50 mm studied on a Nonius CAD4 diffractometer. The unit cell parameters were refined from setting angles of 25 selected reflections ($17.0 < \theta < 70.0$). The intensities were collected using ω-θ scan in the range $1 < \theta < 73°$. Among the 2173 independent reflections, only 1876 were considered as observed according to the condition $I > 3\sigma(I)$. The intensity data were corrected for Lorentz and polarization. The data were corrected for absorption by means of an empirical method from ψ scan concerning 9 high χ reflections ($\chi > 80°$). The structure was solved by means of Multan. Full matrix refinements based on Fo were performed, weighted by $w = 1/\sigma^2(Fo)$. All the hydrogen atoms were located from ΔF syntheses. The final refinement involved the x, y, z, β_{ij} parameters for the non-hydrogen atoms and the x, y, z, B for the hydrogen atoms. The final agreements were $R = 0.051$ and $R_w = 0.071$. Computing by means of Enraf-Nonius SDP system (B.A. Frenz & Associates inc., SDP Structure Determination Package, College Station, texas, USA, 1982) on Micro Vax 3100-80 (Centre de Diffractométrie Automatique de l'Université Claude Bernard, Lyon I). Drawing by means of PLUTO (W. D. S. Motherwell & W. Clegg, PLUTO Program for Plotting molecular and crystal structures, University of Cambridge, England, 1978).

Table 2. Relative Atomic Coordinates and Thermal B_{eq} Parameters of non-Hydrogen Atoms with their Standard Deviations in Parentheses. $B_{eq} = 4/3\ \Sigma i\ \Sigma j\ \beta_{ij}\ a_i\ a_j$

Atom	x	y	z	B_{eq} (Å^2)
S	0.4351(1)	0.39569(9)	0.36595(7)	3.06(2)
C1	-0.1441(5)	0.4975(4)	0.2764(3)	3.36(9)
C2	-0.2243(6)	0.5588(4)	0.1828(3)	3.9(1)
C3	-0.1040(6)	0.5747(4)	0.1392(3)	3.8(1)
C4	0.1030(5)	0.5263(4)	0.1919(3)	3.13(8)
C6	0.5305(5)	0.2832(3)	0.5542(3)	3.03(8)
C7	0.4661(6)	0.2531(4)	0.6212(3)	3.62(9)
C8	0.2602(6)	0.2869(4)	0.5929(3)	3.74(9)
C9	0.1216(5)	0.3493(4)	0.5003(3)	3.40(8)
C10	0.1813(5)	0.3812(3)	0.4311(3)	2.78(8)
C11	0.3876(5)	0.3465(3)	0.4609(2)	2.71(7)
C12	0.0638(5)	0.4481(3)	0.3317(3)	2.80(8)
C13	0.1815(5)	0.4641(3)	0.2861(3)	2.77(8)
C14	0.7517(6)	0.2483(4)	0.5842(3)	4.0(1)
C15	0.2360(6)	0.5437(4)	0.1476(3)	4.1(1)

Table 3. Bond Lengths (Å) and Bond Angles (°) with their Standard Deviations in Parentheses

	Distance		Distance		Distance
S-C11	1.754(5)	C4-C13	1.372(5)	C8-C9	1.358(5)
S-C13	1.755(3)	C4-C15	1.512(7)	C9-C10	1.401(7)
C1-C2	1.358(6)	C6-C7	1.393(7)	C10-C11	1.414(5)
C1-C12	1.407(5)	C6-C11	1.376(4)	C10-C12	1.436(5)
C2-C3	1.412(8)	C6-C14	1.519(6)	C12-C13	1.419(7)
C3-C4	1.400(5)	C7-C8	1.416(6)		

	Angle		Angle		Angle
C11-S-C13	92.1(2)	**C7-C6-C14**	120.9(3)	**S-C11-C6**	125.6(3)
C2-C1-C12	119.5(4)	**C11-C6-C14**	121.5(4)	**S-C11-C10**	111.5(2)
C1-C2-C3	121.6(4)	**C6-C7-C8**	120.4(3)	**C6-C11-C10**	122.9(4)
C2-C3-C4	120.3(4)	**C7-C8-C9**	121.0(5)	**C1-C12-C10**	129.3(4)
C3-C4-C13	117.5(4)	**C8-C9-C10**	120.1(4)	**C1-C12-C13**	118.0(3)
C3-C4-C15	121.1(4)	**C9-C10-C11**	118.0(3)	**C10-C12-C13**	112.6(3)
C13-C4-C15	121.4(3)	**C9-C10-C12**	129.4(3)	**S-C13-C4**	125.7(4)
C7-C6-C11	117.6(4)	**C11-C10-C12**	112.6(4)	**S-C13-C12**	111.2(2)
				C4-C13-C12	123.0(3)

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