Synthesis of some dibenzothiophene-derived sulfur compounds

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Abstract

Some dibenzothiophene deriving sulphur compounds were successful synthesized at laboratory scale by multistep methods. The yield of products decreased after every synthetic step, therefore, the procedures should be strictly followed, especially the refining steps. The products were analysed by GC-MS and the melting points were measured. Results showed that all final products have high purity (98 - 100%).

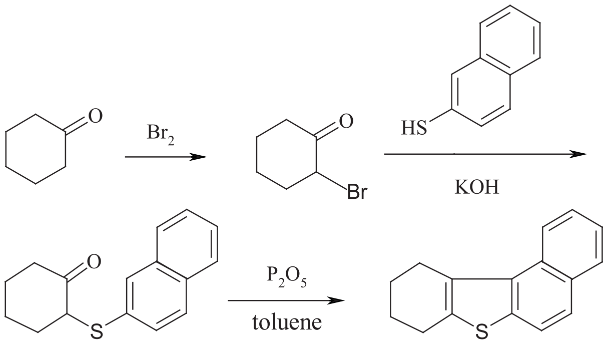
1. Introduction

Sulfur compounds in petroleum lead to equipment corrosion and SOx emissions that cause air pollution and acid rain. In recent years, regulations on sulfur limits of fuel are increasingly strict [1]. Therefore, extensive research has been carried out during the past decades in industrial and academic research laboratories to deeply desulfurize fuels [2, 3]. In laboratory investigations of desulfurization in petroleum, sulfur compounds are mixed in model oil at specific concentrations and then removed [4, 5].

However, many complex dibenzothiophene-derived sulphur compounds are rarely available to purchase. Therefore, this present work investigates the synthesis of some complex sulfur compounds (Table 1).

2. Experimental procedure and Results

2.1. Synthesis of 8, 9, 10, 11- tetrahydro benzo[b] naphtho[2, 1-d]thiophene



Scheme. 1. *Synthesis of 8, 9, 10, 11- tetrahydro benzo[b] naphtho[2, 1-d]thiophene [6, 7]*

Table 1. *Sulfur compounds synthesized in this work*

N_0	Compound	Molecular formula	Molecular weight	wt % S
1	8, 9, 10, 11- tetrahydro benzo[b]naphtho[2, 1-d]thiophene	$C_{16}H_{10}S$	234	13.67
2	7, 8, 9, 10- tetrahydro benzo[b]naphtho[1, 2-d]thiophene	$C_{16}H_{10}S$	234	13.44
3	4-Keto-1, 2, 3, 4-tetrahydro benzo[b]naphtho[2, 3-d]thiophene	$C_{16}H_9SO$	252	12.69
4	4, 6-dimethylbibenzothiophene (4, 6-DMDBT)	$C_{14}H_{12}S$	212	15.09
5	2, 4, 6, 8-tetramethyldibenzothiophene (2, 4, 6, 8-teMDBT)	$C_{16}H_{16}S$	240	13.33

2.1.1. 2-Bromocyclohexanone

24.5g (250mmol) of cyclohexanone was mixed with 150ml of methanol and cooled to -10°C. 40.g (250mmol), bromine was added quickly to the vigorously stirred solution. There was no noticeable exothermic effect. After 30 minutes, the temperature was raised to 0°C. Stirring was continued for 8 hours during which the reaction mixture went up to room temperature. The solution became colourless. The reaction was quenched with 75ml of water. The mixture was stirred overnight at room temperature. An additional 75ml of water was added and the two-phase mixture was concentrated under reduced pressure to remove methanol. The remaining mixture was extracted with 2 * 100ml portions of 1:1 v/v ethyl acetate: hexane. The combined extracts were washed with 70ml of water, 30ml of 1.2M sodium bicarbonate and 75ml of saturated brine and were then dried over anhydrous sodium sulfate. The dry extract was concentrated under reduced pressure and the residue was distilled under vacuum (52°C at 0,1mm) to yield 22g of a colorless liquid (yield = 49.7%). The product should be stored at -10°C under argon.

2.2.1. 2- (ß-naphthylmercapto) cyclohexanone

10.6g 2-bromocyclohexanone (60mmol) was gradually added to an ice-cooled (20°C) solution of ß-thionaphthol (9.4g or 58.75mmol) in 35% aqueous sodium hydroxide (68ml) during 10 minutes under vigorous stirring. After stirring for 1.5 hours, the mixture was diluted with water and extracted with ether. The extract was washed with alkali, water and dried. Removal of ether gave 8g of a dark colour liquid (yield = 54%).

Note: ether was added gradually until no more solid appeared.

2.2.3. 8, 9, 10, 11-tetrahydro-benzo[b]naphtho[1, 2-d] thiophene

The mixture of 8g (ß-naphthylmercapto) cyclohexanone and 24g phosphrous pentoxide was boiled in 160ml of toluene for 1.5 hours. Removal of toluene gave yellow-coloured oil. Recrystallization from alcohol gave 3.2g lustrous needles with melting point of 81°C, purity of 98%, and yield of 43%.

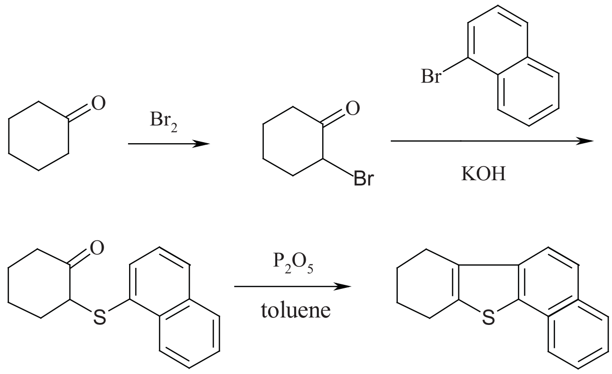
2.2. Synthesis of 7, 8, 9, 10- tetrahydro benzo[b] naphtho[1, 2-d]thiophene

2.2.1. 2 (ß -naphthylmercapto)cyclohexanone

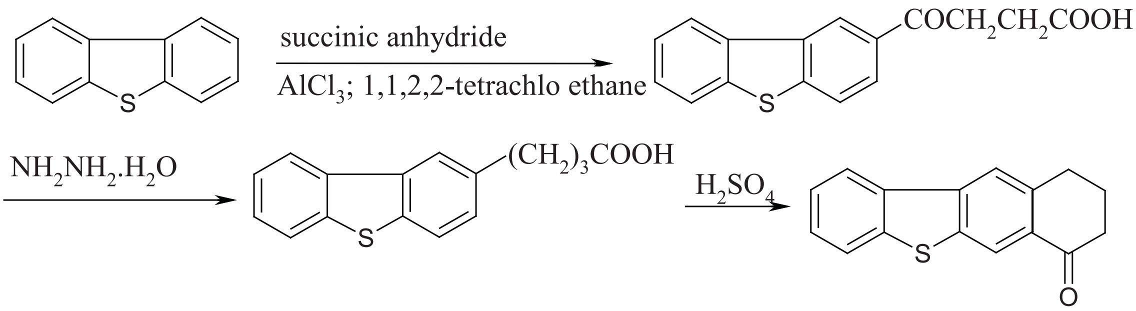
A mixture of ß-thionaphthol (9.2g or 57.5mmol), sodium (1.4g), absolute alcohol (5ml) and 2-bromocyclohexanone (12g or 67.8mmol) was refluxed for 7 hours. The product was extracted with ether. Removal of ether gave 6.5g brown oil (yield = 44.8%).

2.2.2. 7, 8, 9, 10-tetrahydro-benzo[b]naphtho[1, 2-d]thiophene

The mixture of 5g (ß-naphthylmercapto)cyclohexanone and 15g phosphorous pentoxide was boiled in 100ml of toluene for 2 hours. Removal of benzene gave yellow



***Scheme. 2**. Synthesis of 7, 8, 9, 10- tetrahydro benzo[b]naphtho[1, 2-d] thiophene [6, 7]*



***Scheme. 3**. Synthesis of 4-Keto-1, 2, 3, 4-tetrahydro benzo[b]naphtho[2,3-d]thiophene [8, 9]*

coloured oil. Recrystallization from alcohol gave 1.5g of lustrous needles (melting point 96.5°C, purity = 98.6%, yield = 32%).

2.3. 4-Keto-1, 2, 3, 4-tetrahydro benzo[b]naphtho[2, 3-d]thiophene

2.3.1. ß-2-Dibenzotheonylpropionic acid

46g (250mmol) of dibenzothiophene, 27.5g (275mmol) of succinic anhydride was dissolved in a mixture of 200ml of 1, 1, 2, 2-tetracloroethane and 100ml of nitrobenzene. 77.5g of aluminium chloride was added in 30 minutes at 0 - 5°C. After stirring for 5 hours at 20°C the reaction mixture was poured in a mixture of ice and hydrochloric acid. Recrystallization from ethyl acetate gives 18g of product with melting point of 157°C and yield of 25%.

2.3.2. γ-2-Dibenzothienylbutyric acid

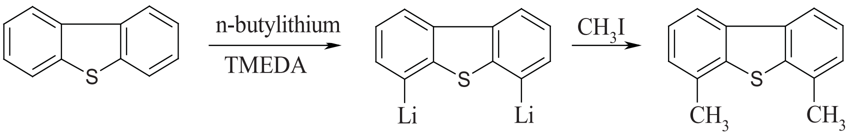
10g (35mmol) of ß-2-dibenzotheonylpropionic acid, 5g of sodium hydroxide, 80ml of 85% hydrazine hydrate were refluxed for 1 hour. Water was then distilled slowly from the reaction mixture until the temperature of the boiling solution reached 195 - 200°C. The mixture was boiled for 3 hours then cooled by the addition of ice. Dilute hydrochloric acid was added slowly with stirring until the solution was acid to litmus. The precipitated product was collected, washed with water, and recrystallized from 80% methanol solution to obtain 4g of product melting at 123°C (yield = 42%).

2.3.3. 4-Keto-1,2,3,4-tetrahydro benzo[b]naphtho[2,3-d] thiophene

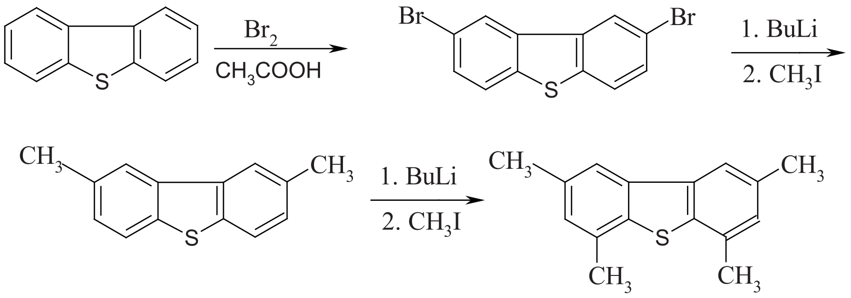
4g (148mmol) of ß-2-dibenzotheonylpropionic acid was stirred with 100ml 98% sulfuric acid for 15 minutes at room temperature. The solution became deep red and was poured in ice. The precipitate was filtered, washed with dilute sodium hydroxide, dried and recrystallized from ethanol to give 0.5g of final product (melting point 175°C, yield = 13%, purity = 98%).

2.4. Synthesis of 4,6-Dimetyl dibenzothiophene

200ml of a 1.6M solution of n-butyllithium in hexane (320mmol) were added drop-wise at 0°C to a solution of TMEDA (320mmol or 37.2g) in 100 ml of dry cyclohexane. After being stirred for 30 minutes at 0°C and 30 minutes at room temperature, the mixture was diluted with 200ml of hexane. Then, 19.6g (106.5mmol) of dibenzothiophene were added. After 2 hours being heated at 60°C, the reaction mixture was cooled at -78 °C and 45.5g of methyl iodide (320mmol) was added in 10 minutes. After completion, the mixture was left for 12 hours at room temperature. It was then poured into a flask containing 1 l of ice-water. The product was extracted with methylene chloride (3 * 250ml). The organic phase was acidified with HCl 1N (300ml) and washed with water (3 * 300ml) and dried over magnesium sulphate. Solvent was removed under vacuum. 4.5g 4, 6-DMDBT (melting at 153 - 157°C) were obtained after recrystallizing from tetrahydrofurane (yield = 22%). Analysis by GC-MS showed that the purity was 99.6%.



Scheme. 4. *Synthesis of 4, 6-Dimetyl dibenzothiophene [10]*



Scheme. 5. *Synthesis of 2, 4, 6, 8 - tetramethyldibenzothiophene (2, 4, 6, 8-TMDBT) [10-12]*

2.5. Synthesis 2, 4, 6, 8-tetramethyldibenzothiophene (2, 4, 6, 8-TMDBT)

2.5.1. Synthesis 2, 8-dibromodibenzothiophene

35.2g (220mmol) of bromine in 100ml of glacial acetic acid were added to a suspension of 10g (54mmol) of dibenzothiophene in 400ml of acetic acid over a period of 30 min. After that, the mixture was stirred for two hours. It was then refluxed over night and cooled. The mixture obtained was yellow. The product was filtered, washed with water and dried.

Recrystallization from acetic anhydride yielded about 10g of material melting at 228 - 230°C (yield = 44.8%).

2.5.2. Synthesis 2, 8-dimethyldibenzothiophene (2, 8-DMDBT)

A solution of n-butyllithium (38.5mmol) in 24ml of hexane was added within 20 min to a stirred suspension of 2, 8-dibromodibenzothiophene (6.6g (19mmol) in 64ml of hexane) at 0°C. The mixture was further stirred for 30 min at 5°C then a yellow solution was obtained. Further stirring for 30 minutes at 18°C was accompanied by the formation of a colourless precipitate. The suspension was cooled at 0°C in an ice bath and methyl iodide (38.7mmol) was added drop-wise. Then the reaction mixture was stirred for 12 hours at room temperature. It was poured into a flask containing 0.32l of ice water. The product was extracted with methylene chloride (3 * 88ml) and solvent was removed under reduced pressure. The final product had a melting point of 119^{o}C and weighed 1g, equivalent to a yield of 25%.

2.5.3. Synthesis of 2, 4, 6, 8-tetramethyldibenzothiophene

20ml of a 1.6M solution of n-butyl lithium in hexane were added drop-wise at 0°C to a solution of TMEDA (3.7g or 0.032mmol in 10ml of dry hexane) under an argon atmosphere. After stirring for 30 minutes at room temperature, the mixture was diluted with 20ml of hexane. Then 2.25g (10.6mmol) of 2, 8-DMDBT were added through a solid addition funnel. After 2 hours heating at 60°C, the reaction mixture was cooled at -78°C and 4.55g of methyl iodide were added gradually. The reaction must be controlled by vigorous agitation and cooling. After completion, the mixture was left for 12 hours at room temperature. It was then poured in to a flask containing 0.1l of ice water. The product was extracted with methylene chloride (3 * 25ml). The organic phase was acidified with HCl 1N (30ml) and washed with water (3 * 30ml), then dried over magnesium sulfate. Solvent was removed under reduced pressure. The product obtained was in colloidal form (1g). Analysis by GC-MS showed that the product contained DBT, 2-MDBT, 2, 8-DMDBT, 2, 6, 8-TMDBT and 2, 4, 6, 8-TMDBT.

3. Conclusion

In this work, all the sulphur compounds were synthesized by complex methods. Therefore, only moderate yields were obtained. However, the observed purity of all final products was from 98 - 100%. Most of these complex sulfur compounds are not available to purchase. After synthesising the compounds were mixed with model diesel and jet fuels for deep desulfurization research [13, 14].

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