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# Chemistry

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## Abstract

## Full Text

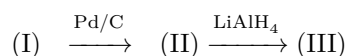
*Chemistry*

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# SYNTHESIS OF 2-METHYL- AND 3-METHYL-1-THIAINDANES AND 2-ETHYLTHIAINDENE

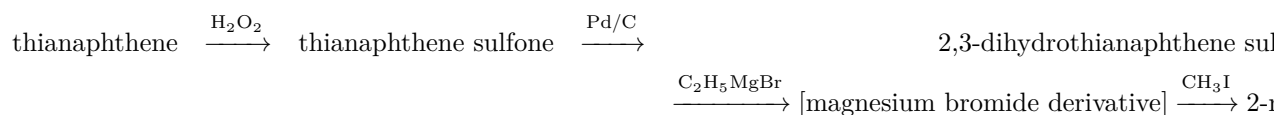
(Presented by Academician A. V. Topchiev, June 14, 1958)

In connection with the study of sulfur compounds of the middle fractions of petroleum, so-called semiaromatic sulfur compounds are of interest as models, in particular alkyl derivatives of 1-thiaindane (2,3-dihydrothianaphthene) with substituents in the five-membered ring. In searching for a method for the synthesis of such compounds, we found that the hitherto unknown\* 2- and 3-methyl-1-thiaindanes (III) can be smoothly obtained by stepwise reduction of the sulfones (I) of the corresponding 2- and 3-methylthiaindenenes:



a)  $R = \text{CH}_3$ ;  $R' = \text{H}$ ;      b)  $R = \text{H}$ ;  $R' = \text{CH}_3$ .

A convenient method for the synthesis of 2-alkylthiaindenenes is the metallation of thiaindene (thianaphthene) with *n*-butyllithium followed by alkylation with dialkyl sulfates. By the action of dimethyl and diethyl sulfate on 2-thiaindenyllithium, 2-methylthiaindene and the previously undescribed 2-ethylthiaindene were obtained, respectively. 2-Methylthiaindene is oxidized by hydrogen peroxide to 2-methylthiaindene sulfone (Ia). The structure of 2-methyl-1-thiaindane (IIIa) was proved by an independent synthesis according to the scheme:



\* We previously showed (1) that, on pyrolysis of allyl phenyl sulfide, not *o*-allylthiophenol with an admixture of 2-methyl-2,3-dihydrothianaphthene is formed, but, contrary to the data of Hurd and Greengard (2), propenyl phenyl sulfide and condensation products of the latter.

3-Methylthiaindene sulfone (Ib) was synthesized according to Werner (3): phenylacetyl sulfide, obtained from chloroacetone and sodium thiophenolate, is cyclized under the action of  $P_2O_5$  with formation of 3-methylthiaindene; the latter is oxidized with  $H_2O_2$  to 3-methylthiaindene sulfone. The structure of 3-methyl-1-thiaindene (IIIb) was proved by hydrodesulfurization over skeletal nickel-cumene was isolated in 84% yield of theory.

0.18 mole of thiaindene is metalated with  $n-C_4H_9Li$  according to (4). To the ethereal solution of 2-thiaindenyllithium is added a solution of 0.18 mole of  $(CH_3)_2SO_4$  in 100 ml of ether, the mixture is stirred for 1 hour and then boiled for 0.5 hour. The ether is distilled off, the residue is added to a solution of  $C_2H_5ONa$  (from 0.1 mole of Na and 120 ml of alcohol) and boiled for 0.5 hour. The mixture is treated with water and extracted with ether. The extracts are distilled in vacuum; 2-methylthiaindene is isolated, yield 91%, b.p. 92–93°/5 mm, m.p. 51–52° (according to (4), m.p. 51.5–52.5°). 0.14 mole of 2-methylthiaindene in glacial  $CH_3COOH$  is oxidized with a 200% excess of 27.3%  $H_2O_2$  for 1 hour at 100°. 2-Methylthiaindene sulfone is obtained, yield 75%, m.p. 109–110° (from alcohol).

Found, %:  $C$  59.89;  $H$  4.44;  $S$  17.47

$C_9H_8SO_2$ . Calculated, %:  $C$  60.00;  $H$  4.44;  $S$  17.77

To an ethereal solution of 2-thiaindenyllithium, obtained from 0.05 mole of thiaindene, is added 0.075 mole of  $(C_2H_5)_2SO_4$  in 50 ml of ether. The mixture is boiled for 10 hours and treated analogously to the preceding; 2-ethylthiaindene is isolated, yield 81%, b.p. 95–96°/1.5 mm,  $n_D^{20}$  1.6063.

Found, %:  $C$  73.93;  $H$  6.31;  $S$  19.72

$C_{10}H_{10}S$ . Calculated, %:  $C$  74.07;  $H$  6.17;  $S$  19.75

2-Ethylthiaindene is oxidized analogously to 2-methylthiaindene; 2-ethylthiaindene sulfone is obtained, yield 77%, m.p. 86.5–87.5° (from alcohol).

Found, %:  $C$  61.86;  $H$  5.15;  $S$  16.31

$C_{10}H_{10}SO_2$ . Calculated, %:  $C$  61.86;  $H$  5.16;  $S$  16.49

A solution of 0.055 mole of 2-methylthiaindene sulfone in 700 ml of alcohol is hydrogenated in the presence of 3 g of 5% Pd/C at an initial  $H_2$  pressure of 50 atm, for 10 hours. The bulk of the alcohol is distilled off, the residue is diluted with water; 2-methyl-1-thiaindene sulfone precipitates, yield 95%, m.p. 115–115.5° (from alcohol).

Found, %:  $C$  59.38;  $H$  5.53;  $S$  17.67;  $M$  182

$C_9H_{10}SO_2$ . Calculated, %:  $C$  59.34;  $H$  5.49;  $S$  17.58;  $M$  182

0.15 mole of 2-methyl-1-thiaindane sulfone in benzene is added to an ethereal solution of 0.23 mole of  $LiAlH_4$  (so that the mixture boils gently) and stirred for 2 hours. The mixture is decomposed with water and steam-distilled; the distillate is extracted with ether. The extracts are dried over  $MgSO_4$  and distilled; 2-methyl-1-thiaindane is obtained, yield 81%, b.p. 118-120°/21 mm,  $n_D^{20.5}$  1.5905. 2-Methyl-1-thiaindane is treated on heating with an alcoholic solution of mercuric chloride; a complex is isolated, yield 80%, m.p. 115-116°. The complex is decomposed with 15% hydrochloric acid, the mixture is steam-distilled, and 2-methyl-1-thiaindane is isolated, yield 45%, b.p. 123°/24.5 mm,  $n_D^{20}$  1.5922,  $d_4^{20}$  1.0859.

Found, %: C 72.04; H 6.70; S 21.08; M 149.8

$C_9H_{10}S$ . Calculated, %: C 72.00; H 6.66; S 21.33; M 150

$MR_D$  found 46.76; calculated 45.94.  $E_{MR_D}$  calculated 0.82.

Thiaindene is oxidized with  $H_2O_2$ , yield of thiaindene sulfone 75%, m.p. 141-142.5° (from alcohol); according to (5) m.p. 142-143°. 0.42 mole of thiaindene sulfone is hydrogenated for 4.5 hours in the presence of 3.5 g of Pd/C at an initial pressure of  $H_2$  of 20 atm. 1-Thiaindane sulfone is isolated, yield 97%, m.p. 90-91° (from alcohol); according to (6) m.p. 91-92°.

To a solution of 2-thiaindanylsulfonylmagnesium bromide in benzene, obtained according to (6) from 0.03 mole of 1-thiaindane sulfone, is added 0.045 mole of  $CH_3J$ .

The mixture is boiled for 4 hours, then treated with water and extracted with benzene. The extracts are dried over  $MgSO_4$ , the solvent is distilled off, and the residue is recrystallized twice from alcohol; 2-methyl-1-thiaindane sulfone is obtained, yield 49% of theory, m.p. 114-115°. A mixed sample with the sulfone obtained by hydrogenation of 2-methylthiaindene sulfone gives no depression of the melting point.

0.08 mole of 3-methylthiaindene sulfone in 750 ml of alcohol is hydrogenated over 8 g of ~7% Pd/C at an initial  $H_2$  pressure of 35 atm for 10 hours; 3-methyl-1-thiaindane sulfone is isolated, yield (crude) 97%, m.p. 57-58° (from alcohol + water, 1 : 3).

Found, %: C 59.50; H 5.58; S 17.28

$C_9H_{10}SO_2$ . Calculated, %: C 59.34; H 5.59; S 17.58

0.22 mole of 3-methyl-1-thiaindane sulfone in ether is added to an ethereal solution of 0.28 mole of  $LiAlH_4$  (with gentle boiling of the ether), stirred for no more than 10 min, and worked up as in the case of 2-methyl-1-thiaindane sulfone; 3-methyl-1-thiaindane is obtained, yield 70%, b.p. 94.5°/4.5 mm,  $n_D^{20}$  1.5953. The complex with  $HgCl_2$ : yield 87%, m.p. 116-116.5° (from alcohol).

Found, %: C 15.52; H 1.48; Hg 57.54

$C_9H_{10}S \cdot 2HgCl_2$ . Calculated, %: C 15.58; H 1.44; Hg 57.86

From the complex, 3-methyl-1-thiaindane is isolated, yield 67%, b.p. 96.5–97°/6 mm,  $n_D^{20}$  1.5969,  $d_4^{20}$  1.0980.

Found, %: C 72.09; H 6.76; S 21.11; M 148.7

C<sub>9</sub>H<sub>10</sub>S. Calculated, %: C 72.00; H 6.66; S 21.33; M 150

$MR_D$  found 46.54; calculated 45.94.  $E_{MR_D}$  calculated 0.60.

3-Methyl-1-thiaindane is oxidized with H<sub>2</sub>O<sub>2</sub>; 3-methyl-1-thiaindane sulfone is isolated, yield 70%.

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*Note: Figure translations are in progress. See original paper for figures.*

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