STUDY OF THE REACTION OF SULFUR WITH ORGANIC COMPOUNDS

XII. The Preparation of Dibenzothiophene, Thianthrene, Di-and Tetramethylthianthrenes and their Sulfides*

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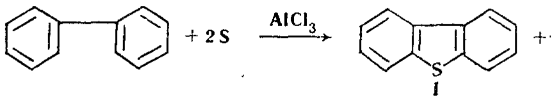
A modified method of synthesizing dibenzothiophene, thianthrene, di- and tetramethylthianthrenes is developed, based on catalytic sulfuration of diphenyl, benzene, toluene, and isomeric xylenes, respectively, in the presence of anhydrous aluminum chloride. The same reaction was used for direct preparation of thianthrene series disulfides.

Dibenzothiophene (I), thianthrene (II), and some of their derivatives are plant growth stimulants and possess bacteriostatic properties [2]. I is also of interest as a fungicide [2, 3], and I and dimethylthianthrene are of interest as insecticides [4]. Di- and tetramethylthianthrenes have been suggested for treating some skin complaints [5].

With a view to making a detailed study of the physiological activities of the above compounds and their sulfides, it appeared to be of interest to develop simple, convenient methods of synthesizing them.

The most practical method of preparing I is based on reaction of diphenyl with sulfur in the presence of anhydrous aluminum chloride

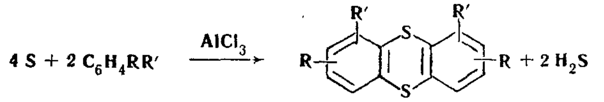


I (1)

It has been shown [12] that at 230–240°, this reaction is complete in 8–10 hours, and that the yield of I obtainable by vacuum-distillation, is 60–80%.

We did not succeed in obtaining such a high yield of I when carrying out the sulfuration of I under the stated conditions (vacuum-fractionation of the reaction products gives a considerable quantity of undistillable tarry residue). Hence we had to make considerable changes in the conditions for synthesizing I. The reaction of diphenyl with sulfur was run in the presence of 10 mole % anhydrous aluminum chloride, at 100–110° for 24–26 hours. The reaction products were decomposed with hydrochloric acid, and the I formed extracted with benzene, thus avoiding the vacuum-distillation step. The yield of I when prepared in this way was 80%.

The product of reaction of elemental sulfur with benzene in the presence of anhydrous aluminum chloride is thianthrene (II) [13–16]:



(2)

R, R' = H (II); R = H, R' = CH$_3$ (III); R, R' = CH$_3$ (IV)

Along with II diphenylsulfide (V) is also formed:

$$2S + 2C_6H_6 \xrightarrow{AlCl_3} \underset{V}{C_6H_5SC_6H_5} + H_2S \qquad (3)$$

At constant S:C_6H_6 ratio the relative yields of II and V are basically determined by the amount of catalyst. We have established the optimum ratio for all three components in the reaction, resulting in II being obtained in 70–80% yield.

The catalytic reaction of sulfur with toluene and all the isomeric xylenes was run under the conditions found, to prepare, according to equation (2), di- (III) and tetramethyl thianthrenes (IV). The method of preparing III and IV by this method was recently patented [6], but pure sulfuration products were not isolated, and they are merely described as forming an oil which does not distil.

III was prepared from toluene and the corresponding tetramethylthianthrenes IVa, IVb, and IVc from o-, m-, and p-xylene. They are not formed as smoothly as II, and the yields do not exceed 30%. IVa and IVc are obtained crystalline (yields 10–15%), while IVb is a liquid (27% yield).

IVc synthesized from xylene is an individual 1, 4, 6, 9-tetramethylthianthrene. IVb obtained from m-xylene can be a mixture of two isomers (1, 3, 6, 8- and 1, 3, 7, 9-tetramethylthianthrenes). In the case of IVa, 4 isomers can be formed (1, 2, 6, 7-, 1, 2, 7, 8-, 1, 2, 8, 9-, and 2, 3, 8, 9-tetramethylthianthrenes), while with III there can even be 6 (1, 6-, 1, 7-, 1, 8-, 1, 9-, 2, 7-, and 2, 8-dimethylthianthrenes). The isomeric compositions of the resultant di- and tetramethylthianthrenes will be given later. Such a complex mixture of isomers with III and IVa made isolation from the reaction products and purification difficult.

On account of the low yields of II, III, and IV, we developed a method of preparing their disulfides

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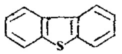
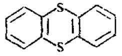
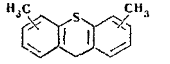
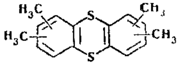
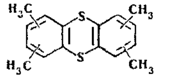
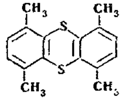
*For Part XI see [1]

Table 1

Run conditions, Melting Points, Analytical Data, and Product Yields in the Sulfuration of Diphenyl, Benzene, Toluene, and Xylenes

Starting hydrocarbon*	Reaction temperature	Reaction time, hr	Reaction product		Mp, °C	Solvent for recrystallizing	Formula	Found, %			Calculated, %			Sulfuration product yield, %
								C	H	S	C	H	S	
Diphenyl	100—110	24—26		(I)	98—99	C_2H_5OH	$C_{12}H_8S$	78.10	4.31	17.12	78.26	4.37	17.37	79
Benzene	80	10		(II)	125	C_2H_5OH	$C_{12}H_8S_2$	66.50	3.71	29.56	66.67	3.72	29.61	74
Toluene	115	8		(III)	190—194 (20 mm)**		$C_{14}H_{12}S_2$	69.24	5.27	26.01	68.80	4.96	26.24	27
o-Xylene	108—134	30		(IVa)	145—146	n-C_6H_{14}	$C_{16}H_{16}S_2$	70.41	6.59	23.24	70.57	6.30	23.13	15
m-Xylene	92—95	30		(IVb)	135—145 (17mm)**		$C_{16}H_{16}S_2$	69.92	6.41	23.24	70.57	6.30	23.13	36
p-Xylene	110—135	50		(IVc)	142	70% CH_3COOH or 70% C_2H_5OH	$C_{16}H_{16}S_2$	70.50	6.19	23.24	70.57	6.30	23.13	20

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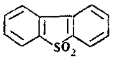
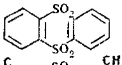
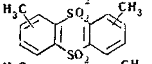
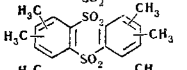
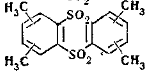
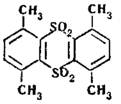
*In the case of diphenyl the molecular ratio is $(C_6H_5)_2$:S:$AlCl_3$ = 2:1:0.1. In the other cases the ratio is arene : S : $AlCl_3$ = 2.8:1:0.1.

**Boiling point.

Table 2

Melting Points, Analytical Data, and Yields of Disulfones Obtained by Oxidizing the Reaction Mixture

Starting hydrocarbon	Sulfone	Mp, °C	Formula	Found, %			Calculated, %			Yield, %
				C	H	S	C	H	S	
Diphenyl	 (VI)	231	$C_{12}H_8SO_2$	—	—	—	—	—	—	80
Benzene	 (VII)	Subl. 281	$C_{12}H_8S_2O_4$	51.69	3.08	22.81	51.47	2.88	22.85	80
Toluene	 (VIII)	137	$C_{14}H_{12}S_2O_4$	54.31	3.84	20.53	54.52	3.92	20.79	40
o-Xylene	 (IXa)	350	$C_{16}H_{16}S_2O_4$	57.27	4.77	18.82	57.12	4.79	19.06	30
m-Xylene	 (IXb)	245—247	$C_{16}H_{16}S_2O_4$	57.01	4.99	18.86	57.12	4.79	19.06	45
p-Xylene	 (IXc)	Subl. 286	$C_{16}H_{16}S_2O_4$	57.27	4.76	18.86	57.12	4.79	19.06	30

directly by oxidizing the crude sulfuration products with hydrogen peroxide. This made it possible to synthesize the disulfones in about 40% yield, appreciably higher (by 10–15%) than when prepared from previously isolated methylthianthrenes.

Run conditions, yields, melting points, and analytical data for I–IV prepared, as well as for their sulfones, are given in Tables 1 and 2.

EXPERIMENTAL

The starting diphenyl, sulfur, and anhydrous $AlCl_3$ were A. R, and were used without further purification. A. R benzene, toluene, o-, m-, and p-xylene were distilled through a column over Na.

Dibenzothiophene (I) and its sulfone (VI). A 250 ml 2-necked flask was fitted with an air condenser and thermometer, and charged with 61.6 g (0.4 mole) diphenyl and 25.6 g (0.8 g at) powdered sulfur. The mixture was heated until it melted, then 5.3 g (0.04 mole) dry $AlCl_3$ was added gradually, and next the whole was heated for 24–26 hr in an oil-bath at 100–120°. After cooling the products were treated with 400 ml 10% HCl, the benzene layer separated off, washed with Na_2CO_3 solution, and then with water, dried over $CaCl_2$, and filtered. The benzene was distilled off, and the residue recrystallized from EtOH.

Yield of I 58.0 g (79%), pale yellow crystals, mp 98–99° (the literature gives [7] mp 99–100°).

Oxidation of I with 30% H_2O_2 in AcOH gave the sulfone VI, mp 231° (the literature [7] gives mp 229–230°).

Thianthrene (II). A 250 ml 2-necked flask, fitted with reflux condenser and thermometer, was charged with 120 ml (1.4 mole) benzene, and 16.0 g (0.5 g at) powdered S. The mixture was heated on a water-bath till the S dissolved, then 6.7 g (0.05 mole) $AlCl_3$ added over an hour. Next the reaction mixture was held at 80° for 10 hr (till H_2S ceased to be evolved), and the products cooled and decomposed with 10% HCl, the benzene layer was separated off, washed with Na_2CO_3 solution, then with water, and dried over $CaCl_2$. The benzene was distilled off, and the residue dissolved in 50 ml boiling dry EtOH. The II which separated on cooling the solution was filtered off with suction, and dried, yield 20.0 g (74%), mp 125° (the literature gives [7] mp 125°).

Dimethylthianthrene (III). Prepared similarly to II. The reaction was run for 8 hr at 110–120°. The reaction products were worked up exactly as described above, and the III thus obtained was vacuum-distilled. It formed a thick oily liquid, bp 190–194° (20 mm), yield 8.2 g (27%).

1, 4, 6, 9-Tetramethylthianthrene (IVc). A mixture of 168.5 ml (1.4 mole) p-xylene and 16.0 g (0.5 mole powdered S was heated at 110–130°, until all the S dissolved, after which 6.7 g (0.05 mole) $AlCl_3$ was added gradually over a period of 1 hr 30 min, and the reaction mixture heated for 50 hr at 110–135°. Excess p-xylene was distilled off, and the residue recrystallized from 70% AcOH, or 70% EtOH. Yield of yellow crystalline IVc, mp 142°, was 6.7 g (19.7%). IVa and IVb were prepared similarly.

Oxidation of II, III, and IV with 30% H_2O_2 in glacial AcOH gave the disulfones (VII, VIII, abd IX). But they were obtained in higher yields by direct oxidation of the crude reaction products.

Thianthrene disulfone (VII). A 250 ml 2-necked flask, fitted with reflux condenser and thermometer, was charged with 120 ml (1.4 mole) benzene and 16.0 g (0.5 g at) powdered S. The mixture was heated on a water-bath till the S dissolved, then 6.7 g (0.05 mole) $AlCl_3$ added gradually. After this the reaction mixture was held at 80° for 10 hr (till H_2S evolution ceased), 100 ml glacial AcOH added and 20 ml 30% H_2O_2, and the whole heated for 3 hr on a water-bath. The products were filtered hot, and the filtrate allowed to cool slowly. 28.0 g minute crystals of VII (80%) separated, recrystallized from glacial AcOH it sublimed at 281°.

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