A STUDY OF THE REACTIONS OF SULFUR WITH ORGANIC COMPOUNDS

XV.* The Action of Sulfur on Exo-Halogen Derivatives of Ethylbenzene and Styrene**

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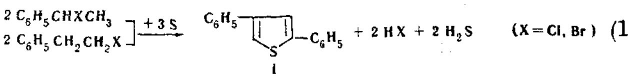
On the basis of the reaction of sulfur with exo-halogen derivatives of ethylbenzene and styrene, new and simple methods of synthesis have been developed for 2,4-diphenylthiophene (from $C_6H_5CHBrCH_3$), 2,5-diphenylthiophene (from $C_6H_5CCl{=}CH_2$), 2,3-dichlorothionaphthene (from $C_6H_5CCl_2CHCl_2$), and the previously unknown dithianaphtheno-[2,3-b;2',3'-e]-1,4-dithiadiene (from $C_6H_5CHClCHClBr$). The latter compound is also formed by the action of sulfur on $C_6H_5CCl_2CH_2Cl$ or $C_6H_5CHClCHCl_2$ in the presence of HBr. The derivatives of thianaphthene obtained have been oxidized to the corresponding sulfones.

In preceding communications [2, 3] we have shown that the reaction of sulfur with phenylhalomethanes can be regarded as a simple method for the synthesis of tetraphenylthiophene (from $C_6H_5CH_2Cl$), thianaphtheno-[3, 2-b]thianaphthene or 2-phenyl-3-chlorothianaphthene (from $C_6H_5CHCl_2$), 2-phenylthianaphthene (from $C_6H_5CHCl_2$), 2-phenylthianaphthene (from $C_6H_5CH_2Br$), and their derivatives. Developing these investigations, we have studied the reaction of sulfur with the exo-chloro and exo-bromo derivatives of ethylbenzene and styrene. On the basis of these investigations we have developed new routes for the synthesis of a number of sulfur-containing heterocycles previously accessible only with difficulty (II, III) or completely unknown (IV).

The reaction of sulfur with 1-halo- or 2-halo-1-phenylethanes at 200°–220° C leads to the formation of 2, 4-diphenylthiophene (I) with a yield of 23%.



(1)

2-Chloro-1-phenylethane, containing the least mobile halogen atom, forms I with a yield of 2–3%.

It must be assumed that when sulfur reacts with halo-1-phenylethanes, styrene is an intermediate that is formed through a sulfur-catalyzed dehydrohalogenation reaction.

$$\left.\begin{array}{l} C_6H_5CHXCH_3 \\ C_6H_5CH_2CH_2X \end{array}\right] \xrightarrow{S} C_6H_5CH{=}CH_2 + HX \qquad (2)$$

Then the styrene reacts with the sulfur, being converted into I (this reaction is well known [4–8]). The action of sulfur on styrene simultaneously forms a small amount of 2, 5-diphenylthiophene [4]. I is also formed by heating sulfur with ethylbenzene, which first dehydrogenates to styrene [9]. We were unable, however, to isolate the styrene as an intermediate product of Reaction (1), apparently because its reaction with sulfur takes place considerably faster than the dehydrohalogenation of the initial phenylhaloethanes (when the latter react with sulfur, HX and H_2S are liberated simultaneously).

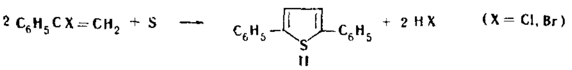
The product of the sulfuration reaction of 1, 2-dichloro-1-phenylethane and 1, 2-dibromo-1-phenylethane is also I, but its yield proved to be lower (18 and 1%, respectively).

$$2\,C_6H_5CHXCH_2X + S \longrightarrow I + 4\,HX \qquad (X = Cl, Br) \qquad (3)$$

Here an intermediate in the reaction is apparently the corresponding β-halostyrene, the reaction of which with sulfur at 210°–230° C also led to I with a yield of about 10%.

$$2\,C_6H_5CH{=}CHX + S \longrightarrow I + 2\,HX \qquad (X = Cl, Br) \qquad (4)$$

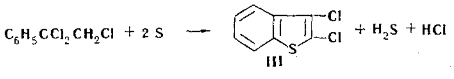
1, 1-Dichloro-1-phenylethane is unstable and readily dehydrochlorinates to α-chlorostyrene on heating. The reaction of the latter with sulfur at 220° C led to the formation of 2, 5-diphenylthiophene (II) with a yield of 8–15%.



(5)

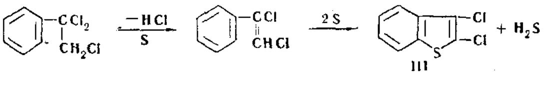
In addition to the latter, I was formed. The molar ratios of II to I were 3:1 (X = Cl) and 3:2 (X = Br).

With sulfur at 225° C, 1, 2, 2-trichloro-1-phenylethane formed 2, 3-dichlorothianaphthene (III) with a yield of 28%.



(6)

We envisage the mechanism of Reaction (6) in the following way:



(7)

And, in fact, the reaction of sulfur with α, β-dichlorostyrene at 220°–230° C led to the formation of III with a yield of 35%.

$$C_6H_5CCl{=}CHCl + 2\,S \longrightarrow III + H_2S \qquad (8)$$

The reaction of sulfur with 1, 2, 2-trichloro-1-phenylethane or with the product of its dehydrochlorination, β, β-dichlorostyrene, at 230°–240° C led to pronounced resinification of the reaction mixture, from which it was impossible to isolate any individual compounds.

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*For communication XIV see [1].

**Presented on 11 May 1966 at the Second Symposium on Organic Compounds of Sulfur at Groningen (Holland).

Table 1

Conditions and Products of the Reaction of Sulfur with exo-Halogen Derivatives of Ethylbenzene and Styrene

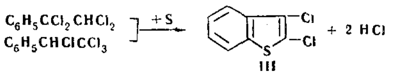
Initial halogen derivative (VI)	Molar ratio VI:S	Solvent*	Reaction temperature, °C	Reaction time, hr	Reaction product	Mp, °C	Empirical formula	Found, %			Calculated, %			Yield, %
								C	H	S	C	H	S	
$C_6H_5CHClCH_3$	2 : 3	—	200—210	6	I	119—120	$C_{16}H_{12}S$	80.91	5.19	13.56	81.35	5.09	13.56	21.3
$C_6H_5CHBrCH_3$	2 : 3	—	200—210	8	I	120—121	$C_{16}H_{12}S$	81.10	5.16	13.41	81.35	5.09	13.56	22.8
$C_6H_5CH_2CH_2Cl$	2 : 3	—	205—220	6	I	120—121	$C_{16}H_{12}S$	81.03	5.10	14.02	81.35	5.09	13.56	2.3
$C_6H_5CH_2CH_2Br$	2 : 3	—	200—225	12	I	119—120	$C_{16}H_{12}S$	81.00	5.15	13.77	81.35	5.09	13.56	20.4
$C_6H_5CHClCH_2Cl$	2 : 1	—	200—205	12	I	122	$C_{16}H_{12}S$	81.16	5.03	13.83	81.35	5.09	13.56	18.6
$C_6H_5CHBrCH_2Br$	2 : 1	—	170—190	3	I	120	$C_{16}H_{12}S$	80.98	5.12	13.98	81.35	5.09	13.56	0.8
$C_6H_5CH{=}CHCl$	2 : 1	T	210—230	4	I	120—121	$C_{16}H_{12}S$	80.93	5.10	13.97	81.35	5.09	13.56	10.3
$C_6H_5CH{=}CHBr$	2 : 1	D	210—225	3	I	121—122	$C_{16}H_{12}S$	81.05	5.23	13.71	81.35	5.09	13.56	10.1
$C_6H_5CCl{=}CH_2$	2 : 1	T	200—220	3	II (I)	152—153	$C_{16}H_{12}S$	81.24	5.13	13.61	81.35	5.09	13.56	15.5 (5.0)
$C_6H_5CBr{=}CH_2$	2 : 1	D	200—225	3	I (II)	120—121	$C_{16}H_{12}S$	81.16	5.13	13.84	81.35	5.09	13.56	12.0 (8.0)
$C_6H_5CCl_2CH_2Cl$	1 : 1	T	220—230	20	III	54	$C_8H_4SCl_2$	47.13	2.03	15.78	47.3	1.97	15.76	28.1
$C_6H_5CCl{=}CHCl$	1 : 1	D	220—235	14	III	54	$C_8H_4SCl_2$	47.28	1.99	15.89	47.3	1.97	15.76	34.6
$C_6H_5CHCl{-}CHCl_2$	1 : 1	T	240	22	Resin									
$C_6H_5CH{=}CCl_2$	1 : 1	D	215—220	12	Resin									
$C_6H_5CCl_2CHCl_2$	1 : 1	D	230—240	20	III	54—55	$C_8H_4SCl_2$	47.34	2.09	15.92	47.3	1.97	15.76	70.8
$C_6H_5CHClCCl_3$	1 : 1	D	230—235	22	III	54—55	$C_8H_4SCl_2$	47.21	2.04	15.86	47.3	1.97	15.76	58.5
$C_6H_5CCl{=}CCl_2$	1 : 1	D	225—240	12	III	54—55	$C_8H_4SCl_2$	47.44	1.91	15.91	47.3	1.97	15.76	65.0
$C_6H_5CCl_2CCl_3$	1 : 3	D	210—230	20	III	54	$C_8H_4SCl_2$	47.29	2.11	15.68	47.3	1.97	15.76	15.8
$C_6H_5CHClCHClBr$	1 : 2	T	220—240	4	IV	209	$C_{16}H_8S_4$	58.39	2.52	38.63	58.55	2.44	39.01	52.4
$C_6H_5CClBrCH_2Cl$	1 : 2	T	220—240	4	IV	208—209	$C_{16}H_8S_4$	58.41	2.34	38.70	58.55	2.44	39.01	35.3
$C_6H_5CCl{=}CHBr$	1 : 2	D	200—220	6	IV	206—208	$C_{16}H_8S_4$	58.83	2.63	38.65	58.55	2.44	39.01	23.2
$C_6H_5CCl_2CH_2Cl$	1 : 2	D***	220—240	15	IV	208	$C_{16}H_8S_4$	58.21	2.03	38.71	58.55	2.44	39.01	33.3
$C_6H_5CHClCHCl_2$	1 : 2	D***	230—240	10	IV	206	$C_{16}H_8S_4$	58.90	2.11	38.83	58.55	2.44	39.01	31.0

*D) *1,2-dichlorobenzene;* T) *1,2,4-trichlorobenzene.*

**Melting points according to the literature: I 120°C [6], II 152-153°C [4], III 55°C [12].

***Hydrogen bromide was passed through the reaction mixture.

The reaction of sulfur with 1, 1, 2, 2-tetrachloro-1-phenylethane or with 1, 2, 2, 2-tetrachloro-1-phenylethane [10] at 230°–240° C gave a particularly high yield of III (60–70%).



III

(9)

In this case, α,β,β-trichlorostyrene may be regarded as an intermediate in Reaction (9). On being heated with sulfur to 225°–240° C, the latter was in fact converted into III (yield 65%).

$$C_6H_5CCl{=}CCl_2 + S \longrightarrow III + HCl \qquad (10)$$

In Reactions (9) and (10), the closure of the thianaphthene ring is accompanied by the evolution of HCl and not H_2S, as in the reaction of sulfur with 1, 2, 2-trichloro-1-phenylethane (7) and with α,β-dichlorostyrene (8). Thus, in the action of sulfur on exo-halogen derivatives of arylalkanes and arylalkenes, the formation of sulfur-containing heterocycles can take place both by a dehydrogenation reaction (with the liberation of H_2S) and by a dehydrohalogenation reaction.

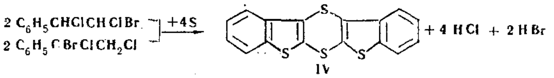
The product of the reaction of pentachloro-1-phenylethane with sulfur at 220°–230° C is also III (yield 16%).

$$C_6H_5CCl_2CCl_3 + 3S \longrightarrow III + S_2Cl_2 + HCl \qquad (11)$$

In this case, in addition to hydrogen chloride, S_2Cl_2 is liberated, formed, apparently, by the dehalogenation with sulfur of the pentachlorophenylethane to α,β,β-trichlorostyrene, which also reacts with sulfur, being converted into III [10].

By oxidation with H_2O_2, III was converted into the sulfone, which possesses effective phytotoxic, fungistatic and fungicidal properties [11, 12].

We have already mentioned [3] that arylbromoalkanes frequently react with sulfur in a direction different from that of chloro derivatives of similar structure. In fact, on reaction with sulfur at 220°–240° C 2-bromo-1, 2-dichloro-1-phenylethane and 1-bromo-1, 2-dichloro-1-phenylethane formed not III but $C_6H_5CCl_2CH_2Cl$ and an unknown compound with the composition $C_{16}H_8S_4$(yields 52 and 35%, respectively). During the reaction HBr and HCl were liberated. We assume that this compound is dithianaphtheno[2, 3-b; 2', 3'-e]-1, 4-dithiadiene (IV), formed in the following way:



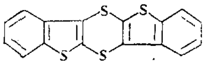
IV

(12)

The same substance (IV) was formed in the reaction of sulfur with α-chloro-β-bromostyrene at 200°–220° C (yield 23%).

$$2\,C_6H_5CCl{=}CHBr + 4\,S \longrightarrow IV + 2\,HCl + 2\,HBr \qquad (13)$$

On oxidation with hydrogen peroxide, IV forms the disulfone. An attempt to split out even one atom of sulfur from IV by heating with copper powder in boiling decalin was unsuccessful (the compound remained unchanged). The absence from the IR spectrum of IV of absorption peaks in the 500–400 cm^{-1} region also confirms that this compound does not contain a disulfide grouping. Absorption bands at 738 and 751 cm^{-1} show the presence in the molecule of IV of a thianaphthene ring substituted in positions 2 and 3 and containing no substituents in the benzene nucleus [13]. The dipole moment of IV is 1.67D, which excludes the possibility of structure V with a different orientation of the thianaphthene rings.



V

We have suggested that the difference in the direction of the reaction of sulfur with bromine-substituted

Table 2

Physical Constants and Methods of Synthesis of exo-Halogen Derivatives of Ethylbenzene and Styrene

Halogen derivatives	Bp, °C (pressure, mm)	n_D^{20}	Method of preparation
$C_6H_5CHClCH_3$	63— 64 (5)	1.5280	$C_6H_5CH_2CH_3+SO_2Cl_2$
$C_6H_5CHBrCH_3$	87 (16)	1.5608	$C_6H_5CH_2CH_3+Br_2$
$C_6H_5CH_2CH_2Cl$	197—198 (760)	1.5294	$C_6H_5CH_2CH_2OH+PCl_5$[15]
$C_6H_5CH_2CH_2Br$	103 (16)	1.5562	$C_6H_5CH_2CH_2OH+HBr$[16]
$C_6H_5CHClCH_2Cl$	115—116 (15)	1.5540	$C_6H_5CH{=}CH_2+Cl_2$[17]
$C_6H_5CHBrCH_2Br$	139—141 (15)	Mp 73—74°	$C_6H_5CH{=}CH_2+Br_2$[18]
$C_6H_5CH{=}CHCl$	103 (33)	1.5780	$C_6H_5CH{=}CHCOOH+Cl_2$[17]
$C_6H_5CH{=}CHBr$	108 (20)	1.6095	$C_6H_5CH{=}CHCOOH+Br_2$[19]
$C_6H_5CCl{=}CH_2$	75— 76 (17)	1.5606	$C_6H_5COCH_3+PCl_5$[20]
$C_6H_5CBr{=}CH_2$	71 (8)	1.5878	$C_6H_5CHBrCH_2Br-HBr$[18]
$C_6H_5CCl_2CH_2Cl$	163—164 (34)	1.5695	$C_6H_5CCl{=}CH_2+Cl_2$[17]
$C_6H_5CCl{=}CHCl$	83— 85 (3)	1.5815	$C_6H_5CCl_2CH_2Cl-HCl$[17]
$C_6H_5CHClCHCl_2$	153 (37)	1.5618	$C_6H_5CH{=}CHCl+Cl_2$[17]
$C_6H_5CH{=}CCl_2$	103 (15)	1.5868	$C_6H_5CHClCHCl_2-HCl$[17]
$C_6H_5CCl_2CHCl_2$	137—138 (10)	1.5715	$C_6H_5CH_2CH_3+SO_2Cl_2$
$C_6H_5CHClCCl_3$*	113—116 (5)	1.5690	$C_6H_5CHOHCCl_3+PCl_5$
$C_6H_5CCl{=}CCl_2$	98 (10)	1.5822	$C_6H_5CCl_2CHCl_2-HCl$[17]
$C_6H_5CCl_2CCl_3$	157—160 (10)	Mp 35°	$C_6H_5CHClCHCl_2+SO_2Cl_2$
$C_6H_5CHClCHClBr$*	184—185 (30)	1.5852	$C_6H_5CH{=}CHBr+Cl_2$
$C_6H_5CClBrCH_2Cl$*	150—153 (28)	1.5738	$C_6H_5CBr{=}CH_2+Cl_2$
$C_6H_5CCl{=}CHBr$*	141—143 (40)	1.6067	$C_6H_5CCl{=}CH_2+Br_2$

*New compound.

arylalkanes and arylalkenes, as compared with the case of the corresponding chlorine derivatives, that is frequently observed is connected with the catalytic influence of the hydrogen bromide liberated in the reaction. And in fact, the product of the reaction of 1, 1, 2-trichloro-1-phenylethane with sulfur at 230°–240° C with the passage of hydrogen bromide through the reaction mixture proved to be not III (which is formed by route (7) in the absence of HBr) but IV (yield 33%).

$$2\,C_6H_5CCl_2CH_2Cl + 4\,S \xrightarrow{HBr} IV + 6\,HCl \qquad (14)$$

The formation of IV in the reaction of sulfur with 1-bromo-1, 2-dichloro-1-phenylethane, an intermediate in which α, β-dichlorostyrene appears, which usually is converted by the action of sulfur into III by route (8), must be explained by the catalytic action of the HBr liberated.

As already mentioned, on being heated with sulfur 1, 2, 2-trichloro-1-phenylethane forms only resinous products. However, when hydrogen bromide was passed through the reaction mixture during its reaction with sulfur at 230°–240° C, IV, was formed with a yield of 31%.

$$2C_6H_5CHClCHCl_2 + 4S \xrightarrow{HBr} IV + 6HCl \qquad (15)$$

The conditions of carrying out the reactions of sulfur with the exo-halogen derivatives of ethylbenzene and styrene, and the melting points, analytical data, and yields of the compounds obtained in this way are given in Table 1.

EXPERIMENTAL

STARTING MATERIALS

1-Chloro-1-phenylethane. A quartz flask fitted with a reflux condenser and a thermometer was charged with 79.6 g (0.75 mole) of ethylbenzene, 33.7 g (0.25 mole) of SO_2Cl_2, 90.0 g of $CHCl_3$, and 0.7 g of PCl_3. The mixture was heated to 80°–90° C and illuminated with ultraviolet light from a PRK-4 lamp (in the absence of traces of mosture) for 7 hr. The solvent and the excess of ethylbenzene were distilled off in the vacuum of a water pump, and the residue was distilled through a column in vacuum. The yield of 1-chloro-1-phenylethane with bp 73°–74° C (5 mm), n_D^{20} 1.5280, was 24.5 g (69.7% calculated on the initial SO_2Cl_2).

1-Bromo-1-phenylethane. A quartz flask fitted with a reflux condenser, dropping funnel, and thermometer, was charged with 212 g (2 mole) of ethylbenzene and was heated to 90°–95° C, and with irradiation with ultraviolet light from a PRK-4 lamp, 160 g (1 mole) of bromine was added in drops. After all the bromine had been added, the reaction mixture was heated and irradiated for another 1 hr, after which it was distilled in vacuum. The yield of 1-bromo-1-phenylethane with bp 87° C (16 mm) was 180 g (64%).

1, 1, 2-Trichloro-1-phenylethane. Dry chlorine was passed into a solution of 69.3 g (0.5 mole) of α-chlorostyrene in 200 ml of chloroform cooled to 0° C until it was no longer absorbed. On the following day the reaction mixture was washed with 5% Na_2CO_3 solution and with water, was dried over $CaCl_2$, and the solvent was distilled off. Distillation of the residue in vacuum gave 57.0 g (77.8%) of 1, 1, 2-trichloro-1-phenylethane with bp 163°–164° C (34 mm), n_D^{20} 1.5695.

1, 1, 2, 2-Tetrachloro-1-phenylethane. A quartz flask fitted with a reflux condenser was charged with a mixture of 53.1 g (0.5 mole) of ethylbenzene, 283.5 g (2.1 mole) of SO_2Cl_2: and 5.7 g of PCl_3, and the mixture was irradiated with ultraviolet light from a PRK-4 lamp at 80°–100° C for 24 hr. After the unchanged SO_2Cl_2 had been driven off, the residue was distilled through a column in vacuum. The yield of 1, 1, 2, 2-tetrachloro-1-phenylethane with bp 137°–138° C (10 mm), n_D^{20} 1.5715, was 38.2 g (31.3%).

1, 2, 2, 2-Tetrachloro-1-phenylethane. A three-necked flask fitted with a stirrer, reflux condenser, and dropping funnel, was charged with a solution of 41.6 g (0.2 mole) of PCl_5 in 150 ml of $CHCl_3$. With stirring, 45.0 g (0.2 mole) of $C_6H_5CHOHCCl_3$ [14] was slowly added. The mixture was heated in the water bath for 2 hr; the solvent and the residual $POCl_3$ were driven off and the residue was distilled through a column in vacuum. The yield of 1, 2, 2, 2-tetrachloro-1-phenylethane with bp 113°–116° C (5 mm) was 36.9 g (75.6%). Found: C 39.00; H 2.71; Cl 58.56%. Calculated for $C_8H_6Cl_4$, %: C 39.39; H 2.48; Cl 58.13.

Phenylpentachloroethane. A three-necked quartz flask fitted with a gas tube, a thermometer, and a reflux condenser was charged with 62.7 g (0.3 mole) of 1, 2, 2-trichloro-1-phenylethane and 0.5 g of PCl. The mixture was heated to 80° C and dry chlorine was passed through it for 18 hr with irradiation with the ultraviolet light from an SVD-120A lamp. The temperature of the reaction mixture gradually rose to 120° C. After this time, the weight of the reaction mixture was 85.0 g. Its distillation in vacuum yielded 62.5 g (74.8%) of phenylpentachloroethane with bp 157°–160° C (10 mm); mp 35° C.

2-Bromo-1, 2-dichloro-1-phenylethane. Dry chlorine was passed into a solution of 91.5 g (0.5 mole) of β-bromostyrene in 200 ml of chloroform cooled to 0° C until a yellow color appeared. On the following day, the reaction mixture was washed with 5% Na_2CO_3 solution and with water and was dried, the solvent was driven off, and the residue was distilled in vacuum. The yield of 2-bromo-1, 2-dichloro-1-phenylethane with bp 184°–185° C (30 mm), n_D^{20} 1.5852, was 92.5 g (72.8%).

1-Bromo-1, 2-dichloro-1-phenylethane was obtained similarly by the chlorination of α-bromostyrene. Yield 76%.

β-Bromo-α-chlorostyrene. With stirring, 80 g (0.5 mole) of bromine was added in drops to a solution of 69.2 g (0.5 mole) of α-chlorostyrene in 200 ml of chloroform cooled to 0° C. On the following day the reaction mixture was washed with 5% Na_2CO_3 solution and water and was dried. The solvent was distilled off and the residue was distilled in vacuum. The yield of β-bromo-α-chlorostyrene with bp 141°–143° C (40 mm), n_D^{20} 1.6067, was 50.9 g (74.6%).

The physical constants of all the exo-halogen derivatives of ethylbenzene and styrene synthesized and the methods of preparing the other starting materials of this type are given in Table 2.

REACTION OF SULFUR WITH EXO-HALOGEN DERIVATIVES OF ETHYLBENZENE AND STYRENE

2, 4-Diphenylthiophene (I). A two-necked flask fitted with a reflux condenser and thermometer was charged with 37.1 g (0.2 mole) of 1-bromo-1-phenylethane and 9.6 g (0.3 g-atom) of sulfur. The reaction mixture was heated to 200°–210° C for 6 hr. After cooling, isopropanol extracted from it crude I which was recrystallized from 80% acetic acid and then from isopropanol (in the presence of 2% of activated carbon). The yield of pure I with mp 122°–123° C was 5.4 g (22.8%). The picrate of I had mp 133°–134° C (according to the literature [21], mp 133°–134° C).

Compound I was obtained similarly from 1-chloro-1-phenylethane, 2-bromo-1-phenylethane, 1, 2-dichloro-1-phenylethane, 1, 2-dibromo-1-phenylethane, β-chlorostyrene, and β-bromostyrene (see Table 1).

2, 5-Diphenylthiophene (II). A solution of 27.7 g (0.2 mole) of α-chlorostyrene in 8 ml of 1, 2, 4-trichlorobenzene was heated with 3.2 g (0.1 g atom) of sulfur for 3 hr. The boiling point of the reaction mixture gradually rose from 170° C to 220° C during this time. The precipitate that deposited on cooling was filtered off and extracted with isopropanol. The II that separated from the alcoholic solution was twice recrystallized from ethanol. The yield of pure II with mp 152°–153° C was 3.5–3.8 g (15–16%). Evaporation of the filtrate yielded 1.2 g (5%) of I with mp 117°–118° C.

In a similar manner, II, was obtained from α-bromostyrene (Table 1).

2,3-Dichlorothianaphthene (III). A solution of 24.4 g (0.1 mole) of 1,1,2,2-tetrachloro-1-phenylethane in 15 ml of 1,2,4-trichlorobenzene was heated with 3.2 g (0.1 g-atom) of sulfur at 230°-240° C until the evolution of HCl had ceased almost completely (20 hr). The reaction mixture was distilled in vacuum. The yield of crude III with bp 145°-155° C (31 mm) was 15.0 g (74.1%). After recrystallization from aqueous ethanol, the yield of pure III with mp 54°-55° C was 14.4 g (70.8%).

In a similar manner, III was obtained from 1,1,2-trichloro-1-phenylethane, 1,2,2,2-tetrachloro-1-phenylethane, α, β, β, -trichlorostyrene, and phenylpentachloroethane (see Table 1). In the last case, S_2Cl_2 was formed as well as III.

Dithianaphtheno[2,3-b;2',3'-e]-1,4-dithiadiene (IV). a) A mixture of 25.4 g (0.1 mole) of 2-bromo-1,2-dichloro-1-phenylethane, 5 ml of 1,2,4-trichlorobenzene, and 6.4 g (0.2 g-atom) of sulfur was heated for 4 hr. The temperature of the reaction mixture was gradually raised from 210° C to 240° C during this time. After cooling, the crude IV was extracted with ethanol and with a mixture of ethanol and benzene. Subsequent recrystallization from a mixture of hexane and benzene (in the presence of 2% of activated carbon) gave 8.6 g (52.4%) of pure IV with mp 209° C.

Similarly, IV was obtained from 1-bromo-1,2-dichloro-1-phenylethane and from β-bromo-α-chlorostyrene (see Table 1).

b) A solution of 20.9 g (0.01 mole) of 1,1,2-trichloro-1-phenylethane in 20 ml of o-dichlorobenzene was heated with 6.4 g (0.2-atom) of sulfur at 230°-240° C for 12 hr with the simultaneous passage of hydrogen bromide through the reaction mixture at the rate of two bubbles per second. The solvent was distilled off and the residue was treated further as described above. The yield of IV with mp 208° C was 5.4 g (33%). IV was obtained from 1,2,2-trichloro-1-phenylethane similarly (yield 31.0%).

PREPARATION OF THE SULFONES III AND IV

2,3-Dichlorothianaphthene sulfone was obtained by Schlesinger and Mowry's method [11]. Its mp of 160°-161° C corresponded to that given inthe literature. Found, %: C 40.90; H 1.89; S 13.68. Calculated for $C_8H_4Cl_2O_2S$, %: C 40.85; H 1.70; S 13.62.

Dithianaphtheno[2,3-b;2',3'-e]-1,4-dithiadiene disulfone. A mixture of 1.6 g (0.005 mole) of IV and a solution of 2 ml of 30% H_2O_2 in 50 ml of glacial acetic acid was heated for 4 hr. The precipitate that deposited on cooling was recrystallized from CH_3COOH. The yield of pure disulfone, in the form of yellow crystals with mp 275°-278° C (decomp) was 0.7 g (36.4%). Found, %: C 48.90; H 2.23; S 32.54. Calculated for $C_{16}H_8S_4O_4$, %: C 48.97; H 2.04; S 32.65.

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