A STUDY OF THE REACTION OF SULFUR WITH ORGANIC COMPOUNDS

XVIII. The Action of Sulfur on alip-Halogen Derivatives of 1,2-Diphenylethane, 1,2-Diphenylethylene, and Tetraphenylethane*

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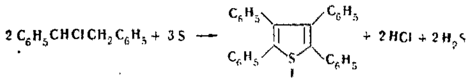
Khimiya Geterotsiklicheskikh Soedinenii, Vol. 6, No. 4, pp. 457–461, 1970

UDC 547.735:542.945.2

The reactions of sulfur with alip-halogen derivatives of 1,2-diphenylethane, 1,2-diphenylethylene, and tetraphenylethane have been studied. A new method for the production of tetraphenylthiophene (from $C_6H_5CHClCHClC_6H_5$), benzothieno[3,2-b]benzothiophene (from $C_6H_5CHClCCl_2C_6H_5$), and of 2-phenylbenzo[b]thiophene (from $C_6H_5CHBrCHBrC_6H_5$) has been developed. On being treated with sulfur, tetraphenyl-1,2-dichloroethane is converted into tetraphenylethylene. 1,2-Diphenylethylene reacts with sulfur in the presence of hydrogen bromide forming 2-phenylbenzo[b]thiophene and tetraphenylthiophene.

Continuing a study of the reaction of elementary sulfur with arylhalogenoalkanes [1–6], we have investigated the sulfidation of alip-halogeno derivatives of 1,2-diphenylethane and of tetraphenylethane.

Heating 1,2-diphenyl-1-chloroethane with sulfur at 220–230° C led to the formation of tetraphenylthiophene (I) with a yield of 32%.



(1)

An intermediate in the reaction is stilbene, into which 1,2-diphenyl-1-chloroethane is converted on heating [7] even in the absence of sulfur. The stilbene then reacts with the sulfur in a known manner [8], being converted into I:

$$2\,C_6H_5CH{=}CHC_6H_5 + 3S \longrightarrow I + 2H_2S \quad (2)$$

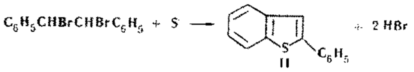
The reaction of sulfur with 1,2-diphenyl-1,2-dichloroethane at 220–240° C also leads to the formation of I, and this with a higher yield (51%):

$$2\,C_6H_5CHClCHClC_6H_5 + S \longrightarrow I + 4HCl \quad (3)$$

An intermediate in Reaction (3) is 1,2-diphenyl-1-chloroethylene, which, with sulfur, in its turn, forms I with a yield of 54%

$$2\,C_6H_5CH{=}CClC_6H_5 + S \longrightarrow I + 2HCl \quad (4)$$

We have already reported [3,4] that arylbromoalkanes frequently react with sulfur in a different direction from that of the chlorine derivatives of analogous structure, which is due to the catalytic influence of the hydrogen bromide liberated in the reaction. In fact, 1,2-diphenyl-1,2-dibromoethane reacts with sulfur at 180–210° C in a direction different from that of the analogous chlorine derivative. The product of the sulfidation reaction in this case is 2-phenylbenzo[b]thiophene (II) (yield 40%):



(5)

In addition to II, I is formed in very low yield.

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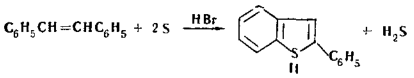
*For part XVII, see [1].

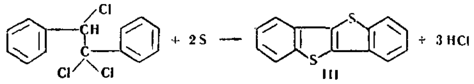
The most sensitive index of the catalytic influence of hydrogen bromide is the sulfidation of 1,2-diphenylethylene (stilbene). The main product of its reaction with sulfur at 220–240° C in a current of HBr is II (yield 30%):


II

(6)

The yield of the I formed simultaneously does not exceed 12%.

The reaction of sulfur with 1,1,2-trichloro-1,2-diphenylethane at 240–260° C led to the formation of benzothieno[3,2-b]benzothiophene (III) with a yield of 48%:


III

(7)

An intermediate in the reaction is apparently 1,2-dichloro-1,2-diphenylethylene, which with sulfur at 250° C forms III with a yield of of 51%:

$$C_6H_5CCl{=}CClC_6H_5 + 2S \longrightarrow III + 2HCl, \qquad (8)$$

The sulfidation of 1,1,2,2-tetrachloro-1,2-diphenylethane at 260° C also led to III with a yield of 50%:

$$C_6H_5CCl_2CCl_2C_6H_5 + 4S \longrightarrow III + 2HCl + S_2Cl_2 \qquad (9)$$

In addition to hydrogen chloride, in this case S_2Cl_2 was liberated, this being formed by the dehalogenation by the sulfur of the tetrachloro-1,2-diphenylethane to 1,2-dichloro-1,2-diphenylethylene, which, with sulfur, forms III by Reaction (8).

By oxidation with H_2O_2, the sulfur-containing heterocyclic compounds I–III obtained were oxidized to the corresponding sulfones.

The product of the reaction of sulfur with 1,2-dichlorotetraphenylethane is tetraphenylethylene (IV) (yield 64%):

$$(C_6H_5)_2CClCCl(C_6H_5)_2 \xrightarrow[-Cl_2]{+S} (C_6H_5)_2C{=}C(C_6H_5)_2 \qquad (10)$$

The possibility of the formation of this compound in the pyrolysis of $(C_6H_5)_2CClCCl(C_6H_5)_2$ is known [9]. In the presence of sulfur, however, this takes place more smoothly and leads to IV in good yield.

The condition for performing the sulfidation reaction and the melting points, analyses, and yields of the compounds obtained are given in Table 1.

EXPERIMENTAL

Starting Materials

1,2-Dichloro-1,2-diphenylethane (synthesized by E. P. Popova). A quartz flask fitted with a reflux condenser was charged with a solution of 18.2 g (0.1 mole) of 1,2-diphenylethane in 75 ml of CCl_4, 67.5 g (0.5 mole) of SO_2Cl_2, and 1.3 g of PCl_3. The mixture was irradiated with ultraviolet light from a PRK-4 lamp and was heated to the boil for 10 hr. The crystals that deposited after cooling were filtered off with suction and recrystallized from ethanol. Yield 18.5 g (73.7%), mp 191–192° C.

1,2-Dibromo-1,2-diphenylethane. A quartz flask fitted with a reflux condenser and dropping funnel was charged with 36.4 g (0.2 mole) of 1,2-diphenylethane in 200 ml of CCl_4. The solution was irradiated with ultraviolet light from a PRK-4 lamp and heated to 50° C, and 64 g (0.4 mole) of bromine and was slowly added to it. After the addition of the bromine, the mixture was irradiated and heated for another 3 hr. The crystals that deposited after cooling were filtered off with suction and recrystallized from ethanol. Yield 49.3 g (72.1%), mp 235° C.

The physical constants and methods of obtaining the other alip-halogen derivatives of 1,2-diphenylethane, 1,2-diphenylethylene, and tetraphenylethane are given in Table 2.

Table 1. Products of the Reaction of Sulfur with alip-Halogen Derivatives of 1,2-Diphenylethane, 1,2-Diphenylethylene, and Tetraphenylethane.

Halogen derivative (V)	Molecular *Ratio:* V S*	Reaction tempera-ture, °C	Reaction *time, hr*	Reaction *product*	Mp, °C**	Empirical formula	Found, %			Calculated, %			Yield, %
							C	H	S	C	H	S	
$C_6H_5CHClCH_2C_6H_5$	2 : 3	220—230	6	I	185	$C_{28}H_{20}S$	86,41	5,03	8,41	86,56	5,19	8,25	32,3
$C_6H_5CHClCHClC_6H_5$	2 : 1	220—240	6	I	185	$C_{28}H_{20}S$	86,68	5,40	8,08	86,56	5,19	8,25	51,1
$C_6H_5CHBrCHBrC_6H_5$	1 : 1	180—210	12	II	175	$C_{14}H_{10}S$	79,86	4,51	15,46	80,0	4,76	15,29	40,7
				I	185	$C_{28}H_{20}S$	86,30	5,11	8,18	86,56	5,19	8,25	5,1
$C_6H_5CH{=}CClC_6H_5$	2 : 1	230—235	4	I	185	$C_{28}H_{20}S$	86,33	5,13	8,41	86,56	5,19	8,25	54,1
$C_6H_5CCl_2CHClC_6H_5$	1 : 2	240—260	12	III	214	$C_{14}H_8S_2$	70,08	3,49	26,79	69,96	3,36	26,68	48,6
$C_6H_5CCl{=}CClC_6H_5$	1 : 2	240—250	8	III	214	$C_{14}H_8S_2$	69,81	3,51	26,51	69,96	3,36	26,68	51,2
$C_6H_5CCl_2CCl_2C_6H_5$	1 : 4	240—260	15	III	214	$C_{14}H_8S_2$	69,90	3,13	26,42	69,96	3,36	26,68	50,0
$(C_6H_5)_2CClCCl(C_6H_5)_2$	2 : 1	200—220	6	IV	224	$C_{26}H_{20}$	93,81	6,18	—	93,97	6,03	—	64,2
$C_6H_5CH{=}CHC_6H_5+HBr$	1 : 2	210—220	8	II	173	$C_{14}H_{10}S$	80,21	4,43	15,03	80,0	4,76	15,24	30,8
				I	184	$C_{28}H_{20}S$	86,83	5,39	8,01	86,56	5,19	8,25	11,9

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*Solvent o-dichlorobenzene. The sulfidation of stilbene was carried out without a solvent.

**Melting points from the literature: I 185° C [2]; II 175° C [3]; III 215° C [2]; IV 223° C [2].

Reaction of Sulfur with alip-Halogen Derivatives of 1,2-Diphenylethane, 1,2-Diphenylethylene, and Tetraphenylethane.

Tetraphenylethiophene (I). A mixture of 25.1 g (0.1 mole) of 1,2-dichloro-1,2-diphenylethane, 5 ml of o-dichlorobenzene, and 1.6 g (0.05 g-atom) of sulfur was heated at 220–230° C for 6 hr. The cooled reaction mixture was washed with ethanol, and the solid residue was recrystallized from a mixture of ethanol and benzene (with the addition of 1% of activated carbon). The yield of pure I with mp 185° C was 9.8 g (51.1%).

Compound I was obtained from 1-chloro-1,2-diphenylethane and from 1- chloro-1,2-diphenylethylene similarly.

Table 2. Physical Constants and Methods of Preparation of the alip-Halogen Derivatives of 1,2-Diphenylethane, 1,2-Diphenylethylene, and Tetraphenylethane

Halogen derivative	Mp, °C	Method of preparation
$C_6H_5CHClCH_2C_6H_5$	Bp 180—184° (16 mm)	$C_6H_5CH_2OH+ZnCl_2+HCl$[7]
$C_6H_5CHClCHClC_6H_5$	191—192	$C_6H_5CH_2CH_2C_6H_5+SO_2Cl_2$
$C_6H_5CHBrCHBrC_6H_5$	237	$C_6H_5CH_2CH_2C_6H_5+Br_2$
$C_6H_5CH{=}CClC_6H_5$	52	$C_6H_5CH_2COC_6H_5+PCl_5$[10]
$C_6H_5CCl_2CHClC_6H_5$	102—103	$C_6H_5CH{=}CClC_6H_5+Cl_2$[10]
$C_6H_5CCl{=}CClC_6H_5$	143—144	$C_6H_5CCl_2CHClC_6H_5-HCl$[10]
$C_6H_5CCl_2CCl_2C_6H_5$	162	$C_6H_5CCl_3+Cu$[11]
$(C_6H_5)_2CClCCl(C_6H_5)_2$	182 (decomp.)	$(C_6H_5)_2C{=}C(C_6H_5)_2+Cl_2$[9]

2-Phenylbenzo[b]thiophene (II). A) A two-necked flask fitted with a reflux condenser and thermometer was charged with a mixture of 34.0 g (0.1 mole) of 1,2-dibromo-1,2-diphenylethane, 20 ml of o-dichlorobenzene, and 3.2 g (0.1 g-atom) of sulfur and was heated at 180–210° C for 12 hr. The solvent was distilled off, and the residue was washed with hexane and filtered off with suction. Its extraction with isopropanol gave 11.5 g of crude II. After recrystallization from isopropanol (with the addition of 1% of activated carbon), 8.5 g (40.7%) of pure II with mp 174–175° C was obtained. The residue after the extraction of II was again extracted with a hot mixture of ethanol and benzene (1 : 1). The microcrystalline I that deposited was recrystallized from the same solvent (with the addition of 2% of activated carbon). The yield of pure I with mp 184° C was 1.0 g (5.1%).

B) A mixture of 18.0 g (0.1 mole) of stilbene and 6.4 g (0.2 g-at) of sulfur was heated to 240° C for 8 hr with the simultaneous passage of gaseous hydrogen bromide through the reaction mixture at the rate of two bubbles per second. Then the reaction mixture was treated as described.above. The II isolated was additionally purified by sublimation. Its yield was 6.4 g (30.8%); mp 173° C. The yield of I with mp 185° C was 2.0 g (11.9%).

Benzothieno[3,2-b]benzothiophene. A mixture of 28.5 g (0.1 mole) of 1,1,2-trichloro-1,2-diphenylethane, 3 ml of o-dichlorobenzene, and 6.4 g (0.2 g-at) of sulfur was heated at 240–260° C for 12 hr. The cooled solidifying mass was ground to a powder and extracted with 80% acetic acid. The microcrystalline III isolated from the extract was recrystallized from acetic acid. The yield of pure III with mp 214° C was 16.5 g (48.6%).

Compound III was obtained by the sulfidation of 1,2-dichloro-1,2-diphenylethylene and tetrachloro-1,2-diphenylethane similarly.

Tetraphenylethylene (IV). 19.6 g (0.05 mole) of 2,2-dichlorotetraphenylethane was heated with 0.8 g (0.025 g-at) of sulfur at 200–220° C for 6 hr. The reaction mixture was cooled and washed with ether. After recrystallization from benzene and treatment with metallic mercury, the yield of pure IV with mp 224° C was 10.3 g (64.2%).

Preparation of sulfones. The sulfones of tetraphenylthiophene (mp 278° C), of 2-phenylbenzo[b]thiophene (mp 174–175° C), and of benzothieno[3,2-b]benzothiophene (mp 270° C) were obtained by oxidation with H_2O_2 in glacial acetic acid [2,3].

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7 October 1968

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