A STUDY OF THE REACTION OF SULFUR WITH ORGANIC COMPOUNDS

XVI.* The Action of Sulfur on exo-Halogen Derivatives of 1,1-Diphenylethane, 1,1-Diphenylethylene, and 1,1,2-Triphenylethane**

M. G. Voronkov and V. E. Udre

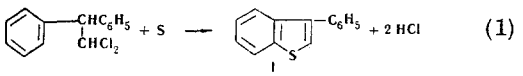
Khimiya Geterotsiklicheskikh Soedinenii, Vol. 4, No. 1, pp. 43–48, 1968

UDC 547.735.737:542.945.22

On the basis of the reaction of elementary sulfur with exo-halogen derivatives of 1,1-diphenylethane, 1,1-diphenylethylene, 1,1,2-triphenylethane, and 1,1,2-triphenylethylene, new and simple methods have been developed for the synthesis of 3-phenylthianaphthene [from $(C_6H_5)_2CHCHCl_2$ or from $(C_6H_5)_2C{=}CHCl$], thianaphtheno[2,3-b]-thianaphthene and its previously unknown 3,8-dihalogen-substituted derivatives [from $(p\text{-}XC_6H_4)_2CHCCl_3$ or $(p\text{-}XC_6H_4)_2C{=}CCl_2$, X = H, Cl, Br], 2,6-dichloro-3-p-chlorophenylthianaphthene [from $(ClC_6H_4)_2CHCCl_3$], and 2,3-diphenylthianaphthene [from $(C_6H_5)_2CClCHClC_6H_5$ or from $(C_6H_5)_2C{=}CClC_6H_5$]. The heterocyclic sulfur compounds synthesized have been oxidized to the corresponding sulfones.

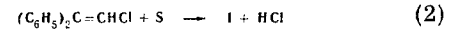
Continuing our investigation of the reaction of arylhaloalkanes with elementary sulfur, affording wide possibilities for the synthesis of various sulfur-containing heterocycles of the aromatic series [1–5], we have studied the reaction of sulfur with exo-halogen derivatives of 1,1-diphenylethane and 1,1,2-triphenylethane.

1-Chloro-2,2-diphenylethane is an unstable compound and is converted into stilbene even on distillation [6]. On being heated with sulfur to 235°–240° C, 1,1-dichloro-2,2-diphenylchloroethane forms 3-phenylthianaphthene (I) with a yield of 53%.



(1)

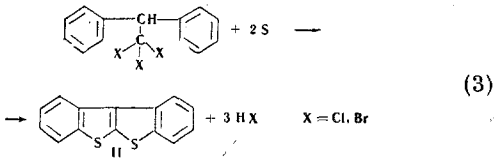
An intermediate in Reaction (1) is 1-chloro-2,2-diphenylethylene, which also forms I with sulfur at 240° C, with a yield of 54%.



(2)

On oxidation with hydrogen peroxide, I is converted into the sulfone.

The reaction of sulfur with 1,1,1-trihalo-2,2-diphenylethanes at 260°–270° C leads to the formation of thianaphtheno[2,3-b]thianaphthene (II) with a yield of 40–50% [7].

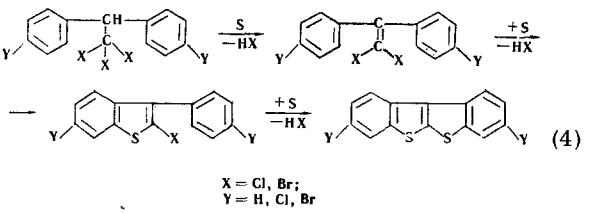


(3)

Up to now, II has been extremely difficult to obtain [8].

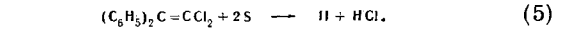
The halogen derivatives of 1,1,1-trichloro-2,2-diphenylethane containing atoms of chlorine or bromine in an aromatic nucleus react with sulfur in a similar manner to (3). Thus, 1,1,1-trichloro-2,2-di-(p-chlorophenyl)ethane and 1,1,1-trichloro-2,2-di(p-bromophenyl)ethane, on being heated with sulfur at 260° C and 220° C, respectively, form 3,8-dichloro- (III) and 3,8-dibromothianaphtheno[2,3-b]thianaphthene (IV) with yields of 50% and 41%.

The mechanism of the formation of II, III, and IV is envisaged by us in the following way.



(4)

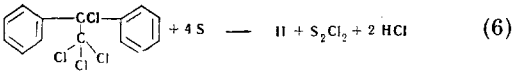
A confirmation of this is the formation of II, yield 54%, in the reaction of sulfur with 1,1-dichloro-2,2-diphenylethylene at 240°–280° C.



(5)

We have also succeeded in isolating with a yield of 40% the previously unknown intermediate product of Reaction (4), 2,6-dichloro-3-p-chlorophenylthianaphthene (V), in the reaction of 1,1,1-trichloro-2,2-di(p-chlorophenyl)ethane with sulfur at 235°–240° C.

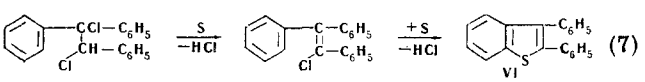
On oxidation with H_2O_2, compounds II and V were converted into the corresponding sulfones. It was impossible to obtain sulfones from compounds III and IV because of their extremely low solubilities. The product of the reaction of tetrachloro-1,1-diphenylethane with sulfur at 220°–240° C is also II (yield 41%).



(6)

In addition to hydrogen chloride, in Reaction (6) S_2Cl_2 is liberated, being formed by the dehalogenation of the tetrachlorodiphenylethane to 1,1-dichloro-2,2-diphenylethylene, which, on being heated with sulfur, forms II by Reaction (5).

1,2-Dichloro-1,1,2-triphenylethane reacts with sulfur at 230°–240° C to give a 52% yield of 2,3-diphenylthianaphthene (VI).



(7)

*For part XV, see [1].

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

Table 1

Conditions and Products of the Reaction of Sulfur with exo-Halogen Derivatives of 1,1-Diphenylethane, 1,1-Diphenylethylene, 1,1,2-Triphenylethane, and 1,1,2-Triphenylethylene

Initial halogen derivative (VII)	Molar ratio of VII to S (solvent, 1, 2-$Cl_2C_6H_4$)	Reaction temperature, ° C	Time of the reaction, hr	Reaction product	Mp, ° C**	Empirical formula	Found, %			Calculated, %			Yield, %
							C	H	S	C	H	S	
$(C_6H_5)_2CHCHCl_2$	1 : 2	235—240	8	I	188—191 (12mm)***	$C_{14}H_{10}S$	80.0	4.19	15.03	80.0	4.76	15.24	53.0
$(C_6H_5)_2C=CHCl$	1 : 2	235—240	6	I	188—191 (12mm)***	$C_{14}H_{10}S$	79.73	4.51	15.41	80.0	4.76	15.24	54.1
$(C_6H_5)_2CHCCl_3$	1 : 2	260—270	8	II	138—139	$C_{14}H_8S_2$	69.84	3.42	26.46	70.01	3.33	26.66	52.1
$(C_6H_5)_2C=CCl_2$	1 : 2	240—280	8	II	139—140	$C_{14}H_8S_2$	69.93	3.56	26.51	70.01	3.33	26.66	54.5
$(p\text{-}ClC_6H_4)_2CHCCl_3$	1 : 2	270—280	6	III*	268	$C_{14}H_6Cl_2S_2$	54.53	1.71	20.49	54.36	1.94	20.39	49.3
$(p\text{-}ClC_6H_4)_2CHCCl_3$	1 : 1	235—240	5	V*	116—117	$C_{14}H_7Cl_3S$	53.36	2.09	10.26	53.62	2.23	10.21	40.4
$(p\text{-}BrC_6H_4)_2CHCCl_3$	1 : 2	215—220	10	IV*	283—284	$C_{14}H_6Br_2S_2$	41.82	1.86	16.30	42.24	1.75	16.07	41.1
$(C_6H_5)_2CHCBr_3$	1 : 2	255—260	4	II	140.5	$C_{14}H_8S_2$	70.13	3.61	26.91	70.01	3.33	26.66	37.5
$(C_6H_5)_2CClCCl_3$	1 : 4	220—235	18	II	140—141	$C_{14}H_8S_2$	69.81	3.01	26.13	70.01	3.33	26.66	41.3
$(C_6H_5)_2CClCHClC_6H_5$	1 : 2	235—240	8	VI	114.5	$C_{20}H_{14}S$	83.72	5.13	11.04	83.88	4.93	11.19	52.4
$(C_6H_5)_2C=CClC_6H_5$	1 : 2	235—245	7	VI	114.5	$C_{20}H_{14}S$	83.81	4.81	11.15	83.88	4.93	11.19	53.8
$(C_6H_5)_2CClCCl_2C_6H_5$	1 : 4	230—240	6	Resin									

*New compound.

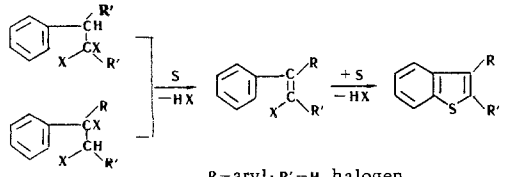
**Literature data: I, bp 100°–120° C (0.1 mm) [10]; II, mp 140.5° C [8]; VI, mp 114°–115° C [9].

***Boiling point.

A confirmation of the intermediate formation of 1-chloro-1,2,2-triphenylethylene is the fact that when the latter is heated with sulfur at 240° C, VI is formed with a yield of 54%. VI has been obtained previously by the thermal decomposition of 1-chloro-1,2,2-triphenylethylene sulfide [9], and it may be assumed that an intermediate in this reaction is 1-chloro-1,2,2-triphenylethylene which reacts with the sulfur liberated and forms VI in accordance with Scheme (7). The oxidation of VI with H_2O_2 led to the sulfone.

The reaction of sulfur with 1,1,2-trichloro-1,2,2-triphenylethane at 230°–250° C was accompanied by pronounced resinification. It was impossible to isolate any individual reaction products from the mixture (including S_2Cl_2).

Thus, the formation of the thianaphthene or the thianaphtheno[2,3-b]-thianaphthene ring in the reaction of exo-halogen derivatives of 1,1-diphenylethane and 1,1,2-triphenylethane with sulfur takes place in all cases via the dehydrohalogenation of the aliphatic part of the molecule and the formation of the corresponding halogen-substituted olefin with the subsequent splitting out of halogen hydride from the molecule of the latter (with the participation of the hydrogen in the ortho position of an aromatic nucleus), this being accompanied by cyclization through the sulfur atom in accordance with the following general scheme.



R = aryl; R′ = H, halogen
aryl; X = Cl, Br

The conditions of performing the sulfuration reaction and the melting points, analytical data, and yields of the compounds obtained are given in Table 1. The products of the oxidation of the sulfur-containing heterocycles synthesized are given in Table 2.

EXPERIMENTAL

The methods of obtaining the initial halogen derivatives that have been described in the literature and their melting points are given in Table 3.

3-Phenylthianaphthene (I). A mixture of 25.1 g (0.1 mole) of 1,1-dichloro-2,2-diphenylethane, 10 ml of 1,2-dichloroethylene, and 3.2 g (0.1 g-atom) of sulfur was charged into a two-necked flask fitted with a reflux condenser and thermometer and was heated at 235°–240° C until the evolution of HCl had ceased completely (about 8 hr). After this, the reaction mixture was distilled in vacuum. The yield of I with mp 189°–193° C (11 mm), n_D^{20} 1.6748, was 11.1 g (53.0%). Compound I was obtained similarly from 1-chloro-2,2-diphenylethylene (yield 54%).

Thianaphtheno[2,3-b]thianaphthene (II). A mixture of 14.3 g (0.05 mole) of 1,1,1-trichloro-2,2-diphenylethane, 2 ml of 1,2-dichlorobenzene, and 3.2 g (0.1 g-atom) of sulfur was charged into a two-necked flask fitted with a reflux condenser and thermometer and was heated at 260°–270° C for 8 hr. The cooled solidified reaction mixture was ground and extracted with isopropanol. Small crystals of II deposited from the alcoholic solution after cooling. After recrystallization from a mixture of ethanol and benzene (with the addition of 1.5% of activated carbon), the yield of pure II with mp 138°–139° C was 5.25 g (52.1%). The picrate of II had mp 147.5° C (literature data [8], 145° C).

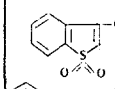
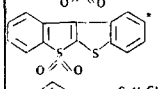
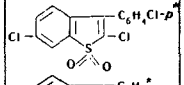
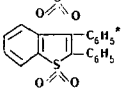
Compound II was obtained similarly from 1,1-dichloro-2,2-diphenylethylene (yield 54%), from 1,1,1,2-tetrachloro-2,2-diphenylethane (41%), and from 1,1,1-tribromo-2,2-diphenylethane (37%).

3,8-Dichlorothianaphtheno[2,3-b]thianaphthene (III). A mixture of 17.72 (0.05 mole) of 1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane, 2 ml of 1,2-dichlorobenzene, and 3.2 g (0.1 g-atom) of sulfur was charged into a two-necked flask fitted with a reflux condenser and thermometer and was heated at 270°–280° C for 6 hr. The reaction mixture was cooled, ground, and extracted with dimethylformamide. On cooling, the solution deposited microcrystalline III, which was purified by sublimation. The yield of pure III with mp 268° C was 7.6 g (49.3%). Compound IV was obtained from 1,1,1-trichloro-2,2-(p-bromophenyl)ethane similarly (yield 41%).

2,6-Dichloro-3-(p-chlorophenyl)thianaphthene (V). A mixture of 17.9 g (0.05 mole) of 1,1,1-trichloro-2,2-bis(p-chlorophenyl)-ethane, 8 ml of 1,2-dichlorobenzene, and 1.6 g (0.05 g-atom) of silver was charged into a two-necked flask fitted with a reflux condenser and thermometer, and was heated at 235°–240° C for 5 hr. The solvent was distilled off in vacuum and the residue was cooled, ground, and extracted with isopropanol. The microcrystalline V isolated from the extract was recrystallized from ethanol. The yield of pure V with mp 116°–117° C was 6.3 g (40.4%).

Table 2

Sulfones obtained by the Oxidation of the Sulfur-containing Heterocyclic Compounds Synthesized

Initial Compound	Sulfone	Mp, ° C	Color of the crystals	Empirical formula	Found, %			Calculated, %			Yield, %
					C	H	S	C	H	S	
I		161—162**	white	$C_{14}H_{10}SO_2$	69.55	4.38	13.30	69.42	4.13	13.22	90.8
II		224—227 (decomp.)	pale yellow	$C_{14}H_8S_2O_2$	61.90	2.92	23.36	61.77	2.94	23.54	61.3
V		216 (decomp.)	yellow	$C_{14}H_7Cl_3SO_2$	48.74	2.12	9.50	48.65	2.03	9.25	54.7
VI		172—173	white	$C_{20}H_{14}SO_2$	75.46	4.57	9.78	75.46	4.43	10.05	81.3

*New compound.

**Literature data [10], mp 161°–162° C.

Table 3

Melting Points and Methods of Preparation of the Initial exo-Halogen Derivatives of 1,1-Diphenylethane, 1,1-Diphenylethylene, 1,1,2-Triphenylethane, and 1,1,2-Triphenylethylene

Halogen derivative	Mp, ° C	Method of preparation
$(C_6H_5)_2CHCHCl_2$	80	$Cl_2CHCH(OC_2H_5)_2+C_6H_6$[11]
$(C_6H_5)_2C=CHCl$	42	$(C_6H_5)_2CHCHCl_2-HCl$[11]
$(C_6H_5)_2CHCCl_3$	64	$Cl_3CCH(OH)_2+C_6H_6$[12]
$(p\text{-}ClC_6H_4)_2CHCCl_3$	105	$Cl_3CCH(OH)_2+C_6H_5Cl$[13]
$(p\text{-}BrC_6H_4)_2CHCCl_3$	139—140	$Cl_3CCH(OH)_2+C_6H_5Br$[13]
$(C_6H_5)_2CHCBr_3$	89	$Br_3CCH(OH)_2+C_6H_6$[14]
$(C_6H_5)_2C=CCl_2$	80	$(C_6H_5)_2CHCCl_3-HCl$[12]
$(C_6H_5)_2CCl-CCl_3$	85	$(C_6H_5)_2C=CCl_2+Cl_2$[15]
$(C_6H_5)_2CCl-CHClC_6H_5$	110—111	$(C_6H_5)_2C=CHC_6H_5+Cl_2$[17]
$(C_6H_5)_2C=CClC_6H_5$	117.5—118	$(C_6H_5)_2CClCHClC_6H_5-HCl$[17]
$(C_6H_5)_2CClCCl_2C_6H_5$	122	$(C_6H_5)_2C=CClC_6H_5+Cl_2$[18]

2,3-Diphenylthianaphthene (VI). A mixture of 32.7 g (0.1 mole) of 1,2-dichloro-1,1,2-triphenylethane, 10 ml of 1,2-dichlorobenzene, and 3.2 g (0.1 g-atom) of sulfur was charged into a two-necked flask fitted with a reflux condenser and thermometer and was heated at 230°-240° C for 8 hr. The reaction mixture was cooled and washed with hexane. The resulting powder was extracted with isopropanol. The VI isolated from the alcoholic solution was recrystallized from ethanol (with the addition of 1% of activated carbon). The yield of pure VI with mp 114.5° C was 15.0 g (52.4%).

Compound VI was obtained similarly with a yield of 53% from 1-chloro-2,2,2-triphenylethylene.

Preparation of the sulfones. The sulfones of 3-phenylthianaphthene, thianaphtheno[2,3-b]thianaphthene, 2,6-dichloro-3-phenylthianaphthene, and 2,3-diphenylthianaphthene (Table 2) were obtained by oxidation with hydrogen peroxide in glacial acetic acid at 100° C by the procedure described previously [2].

REFERENCES

1. M. G. Voronkov, V. E. Udre, and E. P. Popova, KhGS [Chemistry of Heterocyclic Compounds], 1003, 1967.

2. M. G. Voronkov and V. E. Udre, KhGS [Chemistry of Heterocyclic Compounds], 148, 683, 1965.

3. M. G. Voronkov and V. E. Udre, KhGS [Chemistry of Heterocyclic Compounds], 527, 1966.

4. M. G. Voronkov, T. V. Lapina, and E. P. Popova, KhGS [Chemistry of Heterocyclic Compounds], 49, 1968.

5. M. G. Voronkov, Izv. AN LatvSSR, 3, 33, 1965.

6. E. Hepp, Ber., 7, 1409, 1874.

7. M. G. Voronkov and V. E. Udre, USSR Authors' Certificate 199909, 1967.

8. R. Mitra, L. Pandya, and B. Tilac, J. Sci. Ind. Res. (India), 16B, 348, 1957; C. A., 52, 5371, 1958.

9. H. Staudinger and J. Siegwart, Helv. Chim. Acta, 3, 840, 1920.

10. O. Dann and M. Kokorudz, Ber., 91, 172, 1958.

11. W. Buttenberg, Ann., 279, 324, 1894.

12. A. Baeyer, Ber., 5, 1098, 1872.

13. O. Zeidler, Ber., 7, 1181, 1874.

14. G. Goldschmiedt, Ber., 6, 985, 1873.

15. H. Biltz, Ber., 26, 1956, 1893.

16. C. Hell and F. Wiegandt, Ber., 37, 1431, 1904.

17. J. van der Kamp and M. Sletzinger, J. Am. Chem. Soc., 63, 1879, 1941.

18. J. Meisenheimer, Ann., 456, 146, 1927.

15 March 1966

Institute of Organic Synthesis, AS LatvSSR, Riga