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INVESTIGATION OF THE REACTION OF SULFUR WITH ORGANIC COMPOUNDS

X. Action of Sulfur on Benzyl Bromide and Its Derivatives*

M. G. Voronkov and V. E. Udre

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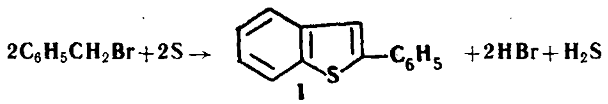
A new simple method of synthesizing 2-phenylthianaphthene and its hitherto unknown 4', 6-dihalogeno derivatives is worked out. It is based on the reaction of sulfur with benzyl bromide, or p-halogenobenzyl bromides. All the compounds of this type synthesized are converted to their sulfones. When benzylidene bromide and o-chlorobenzyl bromide are heated with sulfur, they give thianaphtheno-[3, 2-b] thianaphthene. Reaction of sulfur with p-chlorobenzyl bromide at 210-230° C, and with the analogous m-chloro-derivative at 190-210°C, gives the corresponding dichlorostilbenzenes. Action of sulfur on p- and o-methylbenzyl bromide (but not on the m-isomer) converts them to the corresponding dimethylstilbenes.

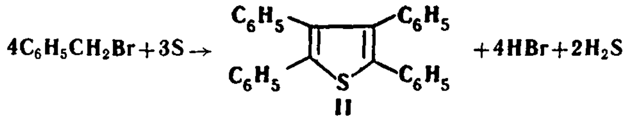
Continuing a study of the action of sulfur on arylhalogenoalkanes [2, 3], the sulfuration of benzyl bromide and its derivatives has now been investigated. In the course of this work, it was unexpectedly shown that phenylbromomethane often reacts with sulfur differently from the chloro compound of analogous structure [3].

Thus, heating benzyl bromide with sulfur at 220°C gives an over 40% yield of 2-phenylthianaphthene (I):



(1)

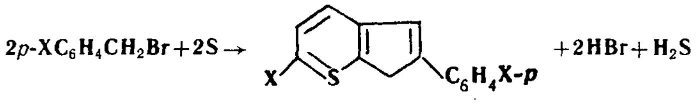
and the only side reaction product is tetraphenylthiophene (II), the yield of which does not exceed 10%:



(2)

The new method of preparing 2-phenylthianaphthene advantageously differs from the existing ones [4, 5] in its extreme simplicity and the accessibility of the starting materials.

1-Chloro- and p-bromobenzylbromide react with sulfur at 180-190°C, to give 20-30% yields of the hitherto unknown 4', 6-dichloro-2-phenylthianaphthene (III) and 4', 6-dibromo-2-phenylthianaphthene (IV), respectively:



$X = Cl$ (III), Br (IV)

(3)

H_2O_2 oxidation converts I, III, and IV into the corresponding sulfones.

At higher temperature (210-230° C), the product of reaction of sulfur with p-chlorobenzyl bromide is 4, 4'-dichlorostilbene (V):

$$2p\text{-}ClC_6H_4CH_2Br \xrightarrow{S} p\text{-}ClC_6H_4CH\underset{V}{=}CHC_6H_4Cl\text{-}p + 2HBr \qquad (4)$$

The yield amounts to 25%.

Unlike the para compound, m-chlorobenzyl bromide and sulfur at 190-210°C give only a little (6-7%) 3, 3'-dichlorostilbene m-$ClC_6H_4CH=CHC_6H_4Cl$-m (VI).

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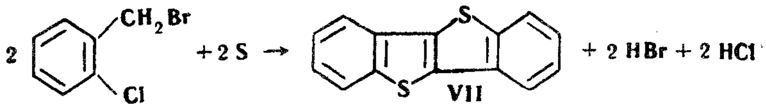
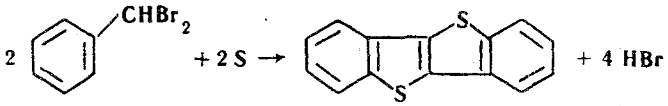
*For Part IX see [1].

Heating o-chlorobenzyl bromide with sulfur converts it into thianaphtheno [3, 2-b] thianaphthene (VII):



VII is also formed by reacting sulfur with benzylidene bromide:



In both cases the yield of VII is about 10%.

Reaction of sulfur with p- and o-methylbenzyl bromide at 220° gives approximately 10% yields of the dimethylstilbenes:

$$2CH_3C_6H_4CH_2Br \xrightarrow{S} CH_3C_6H_4CH{=}CHC_6H_4CH_3 + 2HBr \qquad (7)$$

Under the conditions investigated, it was not possible to obtain the corresponding dimethyl derivatives of 2-phenylthianaphthene from methylbenzylbromides by the reaction of Eq. (3) where X = Me.

Table 1 gives melting points, analytical data, and yields for all compounds obtained by reacting sulfur with benzyl bromide and its derivatives. Table 2 gives analogous data for the products of oxidation of the heterocyclic sulphur compounds synthesized.

Experimental

Benzyl bromide. A 3-necked quartz flask, fitted with a reflux condenser, dropping funnel, and thermometer, was charged with 184 g (2 mole) toluene, which was heated to 90°C, irradiated with UV light from a PRK-4 lamp, and 160 g (1 mole) bromine dropped in. After all the bromine had been added, heating and irradiation were continued for a further hour, after which the products were distilled, to give 108 g (63%) benzyl bromide, bp 198–199°C, n_D^{20} 1.5742.

Similar bromination of the appropriate chloro- and bromo-toluenes and xylenes gave p-, m-, and o-chlorobenzyl bromides, p-bromobenzyl bromide, p-, o-, and m-methylbenzyl bromides.

Benzylidene bromide. 320 g (2 mole) bromine was added dropwise to 92 g (1 mole) toluene which was irradiated with UV light, and held at 100°C. Irradiation and heating were continued for 2 hr after all the bromine had been added. Vacuum-distillation gave 105 g (41.9%) benzylidene bromide bp 136° C (33 mm).

Table 3 gives the physical constants of all the starting compounds.

Reaction of sulfur with benzyl bromide and its derivatives

2-Phenylthianaphthene (I) and tetraphenylthiophene (II). A 2-necked flask was fitted with a reflux condenser and thermometer, and in it placed 17.1 g (0.1 mole) benzyl bromide and 3.2 g (0.1 g at) S. The mixture was heated, keeping the temperature below 220°C (about 1 hr), then for 3 hr at 220–230°C. After cooling, the reaction products were extracted with iso-PrOH, and gave 6.4 g crude I. Recrystallization from 80% AcOH, followed by repeated crystallization from iso-PrOH, gave 4.4 g (42%) pure I, mp 174–175° C.

The residue remaining after extracting I was recrystallized from boiling EtOH-benzene with 3% activated charcoal, and gave 0.8 g (8.1%) pure II, mp 185° C.

4', 6'-Dichloro-2-phenylthianaphthene (III). 41.0 g (0.2 mole) p-chlorobenzyl bromide and 3 ml mesitylene were heated together with 4.8 g (0.15 g at) S, for 2.5 hr at 180–190° C. Extraction of the reaction products with iso-PrOH gave 10.2 g crude III, purified by recrystallization from hexane-benzene. Yield of pure III, mp 192–193° C, 5.9 g (28.2%, based on the S reacted).

4', 6-Dibromo-2-phenylthianaphthene (IV). 25.0 g (0.1 mole) p-bromobenzyl bromide and 2 ml mesitylene were heated with 2.4 g (0.075 g at) S at 180–190° for one hr, and then for 4 hr at 150–160°. Extraction of the reaction products with iso-PrOH gave 5.0 g crude IV. It was recrystallized, first from hexane-benzene, then from AcOH. Yield of pure IV, mp 212° C, 285 g (21% based on the S reacted).

Table 1

Reaction of Sulfur with Benzyl Bromide and its Derivatives: Conditions and Reaction Products

Starting benzyl bromide (X)	Molar ratio X:S	Reaction temperature °C	Reaction time, hr	Reaction product	Mp**	Formula	Found, %			Calculated, %			Yield, %
							C	H	S	C	H	S	
$C_6H_5CH_2Br$	1 : 1	220	4	I	174—175	$C_{14}H_{10}S$	79.69	4.86	15.11	80.0	4.76	15.24	42.0
	1 : 1	220	4	II	185	$C_{28}H_{20}S$	86.41	5.09	8.28	86.56	5.19	8.25	8.1
p-$ClC_6H_4CH_2Br$	4 : 3	180—190	2,5	III*	192—193	$C_{14}H_8Cl_2S$	60.43	3.10	11.29	60.21	2.97	11.47	28.2
	1 : 1	190—210	6	V	174—175	$C_{14}H_{10}Cl_2$	67.21	3.88		67.47	4.01		
p-$BrC_6H_4CH_2Br$	4 : 3	180—190	2	IV*	212	$C_{14}H_8Br_2S$	45.93	2.35	8.35	45.69	2.19	8.71	21.0
m-$ClC_6H_4CH_2Br$	1 : 1	190—210	3	VI	86—87	$C_{14}H_{10}Cl_2$	67.19	3.93		67.47	4.01		23.7
o-$ClC_6H_4CH_2Br$	1 : 1	205—215	5	VII	216	$C_{14}H_8S_2$	70.01	3.33	26.46	69.96	3.36	26.68	3.4
$C_6H_5CHBr_2$	1 : 1	170—185	2	VII	215,5	$C_{14}H_8S_2$	69.91	3.39	26.61	69.96	3.36	26.68	9.1
p-$CH_3C_6H_4CH_2Br$	1 : 1	190—200	4	VIII	175—176	$C_{16}H_{16}$	92.12	7.83		92.31	7.69		11.5
o-$CH_3C_6H_4CH_2Br$	1 : 1	190—200	4	IX	80—81	$C_{16}H_{16}$	92.01	7.80		92.31	7.69		10.5
m-$CH_3C_6H_4CH_2Br$	1 : 1	190—210	3		Resin								

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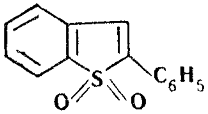
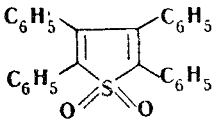
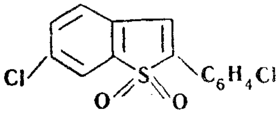
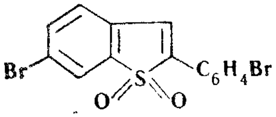
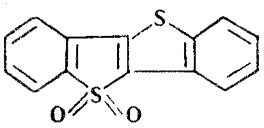
* New compound

** Literature mps: I) 174-175° [4]; II) 185° [3]; V) 177° [5]; IV) 215.5° [3]; VIII) 179° [7]; IX) 82° C [8].

Table 2

Sulfones Obtained by Oxidizing the Synthetic Heterocyclic Sulfur Compounds

Starting compound	Sulfone		Mp** ° C	Color of crystals	Formula	Found, %			Calculated, %			Yield, %
						C	H	S	C	H	S	
I		XI*	176—177	Yellowish	$C_{14}H_{10}SO_2$	69.53	4.32	12.99	69.42	4.13	13.22	38.2
II		XII	275—277	Bright yellow	$C_{28}H_{20}SO_2$	80.06	4.37	7.89	80.0	4.76	7.62	64.9
III		XIII*	242	Yellowish	$C_{14}H_8Cl_2SO_2$	53.85	2.59	9.99	54.0	2.57	10.29	36.8
IV		XIV*	265 (decomp)	Yellowish	$C_{14}H_8Br_2SO_2$	42.31	2.14	7.79	42.0	2.02	8.01	32.1
VII		XV	270 (decomp)	Bright yellow	$C_{14}H_8S_2O_2$	61.91	3.03	23.68	61.77	2.94	23.54	56.7

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* New compound.

** Literature melting points [3]: XII) 275–277°; XV) 270° C (decomp).

Table 3

Physical Constants of the Starting Benzyl Bromides (X)

x	Bp °C (pressure mm)	n_D^{20}	Mp °C
$C_6H_5CH_2Br$	198—199	1.5742	
p-$ClC_6H_4CH_2Br$	111—113 (14)	—	51
m-$ClC_6H_4CH_2Br$	137 (37)	1.5898	
o-$ClC_6H_4CH_2Br$	132 (33)	1.5923	
p-$BrC_6H_4CH_2Br$	154 (34)	—	63
p-$CH_3C_6H_4CH_2Br$	218—220 (740)	—	35
m-$CH_3C_6H_4CH_2Br$	106 (21)	1.5642	
o-$CH_3C_6H_4CH_2Br$	118 (33)	1.5760	
$C_6H_5CHBr_2$	136 (33)	1.6152	

Thionaphtheno [3, 2-b] thianaphthene (VII). a) 41.0 g (0.2 mole) o-chlorobenzyl bromide was heated with 6.4g (0.2 gr at) S at 205–220° C for 5 hr. Crude VII was obtained by extracting the reaction products with EtOH and EtOH-benzene. It was recrystallized from hexane-benzene with the addition of 3% active charcoal. Yield of pure VII mp 216° C, 2.2 g (9.1%).

b) 25.0 g (0.1 mole) benzylidene bromide and 3 ml mesitylene were heated with 3.2 g (0.1 g at) S for 2 hr at 170–185° C. Extraction of the reaction products with AcOH gave crude VII, which was purified by sublimation, mp 215.5° C, yield 1.9 g (8.6%).

4, 4'-Dichlorostilbene (V). 41.1 g (0.2 mole) p-chlorobenzyl bromide was heated with 6.4 g (0.2 g at) S for 6 hr at 190–210° C. The reaction products were extracted with iso-PrOH, and the V obtained recrystallized from EtOH, yield of pure V, mp 174–175° C, 5.9 g (23.7%).

3, 3'-Dichlorostilbene (VI). 20.5 g (0.1 mole) m-chlorobenzyl bromide and 2 ml mesitylene were heated together with 3.2 g (0.1 g at) S at 190–210° C for 3 hr. The mesitylene and unreacted m-chlorobenzyl bromide were vacuum-distilled off, and the residue extracted with EtOH, 20 ml water added to the extract, and the mixture left for 48 hr. Yield of pure VI mp 86–87° C, 0.8 g (6.4%).

4, 4'-Dimethylstilbene (VIII). 18.5 g (0.1 mole) p-methylbenzyl bromide and 3 ml mesitylene were heated with 3.2 g (0.1 g at) S at 190–200° C for 4 hr. The unreacted starting materials were vacuum-distilled off, and the residue extracted with AcOH. The crude VIII was recrystallized from EtOH. Yield of pure VIII, mp 174–175° C, 1.2 g (11.5%).

2, 2'-Dimethylstilbene (IX). A mixture of 18.5 g (0.1 mole) o-methylbenzyl bromide, 4 ml mesitylene, and 3.2 g (0.1 g at) S was heated for 4 hr at 190–200° C. Vacuum-distillation gave 1.4 g IX bp 180–200° C (35 mm), recrystallized from aqueous EtOH. Yield of pure IX, mp 80–81° C, 1.1 g (10.5%).

Under similar conditions, m-methylbenzyl bromide and S gave only resinous compounds.

Preparation of sulfones

Sulfone of 4', 6-dichloro-2-phenylthianaphthene (XIII). 1.39 g (0.005 mole) III was heated with a solution of 2.2 g (0.025 mole) 30% H_2O_2 in 50 ml glacial AcOH for 4 hr. The crystalline precipitate of XIII formed on cooling was recrystallized from AcOH. Yield of pure XIII, mp 242° C, 0.57 g.

The sulfones XII, XIV, and XV were obtained similarly. The sulfone XI was isolated from the reaction products by adding water, and was purified by recrystallizing from EtOH.

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Institute of Organic Synthesis, AS LatvSSR,
Riga