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STUDY OF THE REACTION OF SULFUR WITH ORGANIC COMPOUNDS

VIII. Reaction of Sulfur with Phenylchloromethanes*

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The reaction of sulfur with phenylchloromethanes of the type $(C_6H_5)_mCCl_nH_{4-m-n}$ ($m = 1$-3; $n \leq 3$) is investigated. New simple methods of synthesizing tetraphenylthiophene (from $C_6H_5CH_2Cl$) and thianaphtheno [3, 2-b] thianapthene or 2-phenyl-3-chlorothianaphthene (from $C_6H_5CHCl_2$) are developed. All the heterocyclic sulfur compounds synthesized are oxidized to the corresponding sulfones. Diphenylchloromethane when heated with sulfur smoothly gives a high yield of tetraphenylethylene, and triphenylchloromethane treated similarly gives triphenylmethane. $C_6H_5CCl_3$ and $(C_6H_5)_2CCl_2$ undergo practically no reaction with sulfur under the conditions investigated.

The action of elementary sulfur organic halogen derivatives has been but little studied. It is known that CCl_4 reacts with sulfur to give $CSCl_2$ and CS_2 [2-4], and that CBr_4 gives CS_2BR_4 and its decomposition products [5]. The action of sulfur on polyfluoroalkyliodides $H(CF_2)_nCH_2I$ gives sulfides and disulfides of the type $[H(CF_2)nCH_2]_2S_m$ ($m = 1, 2$) [6]. Hexachloro- and hexafluoropropene react with sulfur to give respectively 3, 3, 4, 5-tetrachloro-1, 2-dithiol [7] and perfluoro-2, 5-dimethyl-1, 4-dithiane [8].

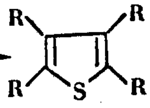
Reaction of halogen derivatives of diolefins with sulfur converts them to cyclic sulfides and disulfides [9]. The reaction of sulfur with some halogen derivatives of diphenyldisulfide and -sulfoxide has been described [10]. The reaction of sulfur with chlorinated hydrocarbons has been patented as a method of preparing artificial resins [11, 12].

Hitherto the reaction of elemental sulfur with phenylchloromethanes has not been studied. It has only been noted [13] that when benzyl chloride is boiled with sulfur it starts to decompose with evolution of H_2S.

A study has now been made of the reaction of sulfur with phenylchloromethanes of the type $(C_6H_5)_mCCl_nH_{4-m-n}$, with $m = 1$-3; $n \leq 3$. These investigations marked a new synthetic route to heterocyclic sulfur compounds with aromatic substituents, or condensed with aromatic rings. Hitherto many compounds of that type have been accessible with difficulty, and have been prepared in very low yield by multistate syntheses [14, 15], or else have not been known.

It was shown by the present authors [16, 17] that the reaction of benzyl chloride with sulfur at 200-240°, which takes place with evolution of HCl and H_2S, smoothly gives a 68% yield of tetraphenylthiophene (I), the equation being

$4RCH_2Cl+3S \longrightarrow$



$+2H_2S+4HCl,$ (1)

I

where R = C_6H_5. Oxidation of I with H_2O_2 gives the corresponding sulfone (II).

It is interesting to note that II is intensely luminescent when irradiated with ultraviolet light, while I is almost completely without luminescent properties.

Previously the most convenient method of preparing I (in about 60% yield) was based on reaction of sulfur with stilbene [14, 18]:

$$2RCH=CHR+3S \rightarrow I+2H_2S' \quad (R=C_6H_5) \qquad (2)$$

It is to be assumed that in the action of sulfur on benzyl chloride stilbene is also an intermediate product, formed through sulfur-catalyzed intermolecular dehydrochlorination:

$$2C_6H_5CH_2Cl \xrightarrow{S} C_6H_5CH=CHC_6H_5+2HCl \qquad (3)$$

Further, stilbene reacts rapidly with sulfur according to equation 2, giving I. The correctness of equation 3 is supported by diphenylchloromethane smoothly dehydrochlorinating on heating with sulfur, to give a 70% yield of tetraphenylethylene (III) **

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[*] For Part VII see [1].

[**] In the absence of sulfur this reaction can be brought about only at 300°, under pressure and in solvent medium.

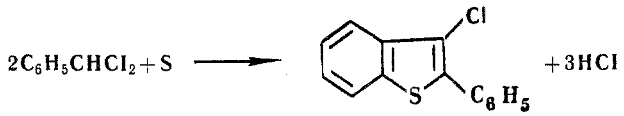
$$2(C_6H_5)_2CHCl \xrightarrow{S} (C_6H_5)_2C{=}C(C_6H_5)_2 + 2HCl \qquad (4)$$

III

The latter, unlike stilbene, reacts with great difficulty with sulfur, so that under the reaction conditions it is unchanged.

Attempts to prepare the corresponding tetraarylthiophenes by reacting sulfur with p-chlorobenzylchloride, and with α-(chloromethyl)-naphthalene terminated unsuccessfully because of tar formation.

The product of reaction of sulfur with benzylidene chloride at 240° is the hitherto unknown 2-phenyl-3-chloro-thianaphthalene (IV), formed in 52% yield [17, 20]:

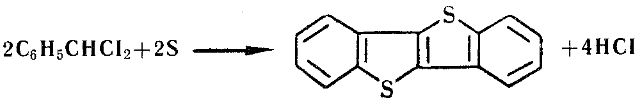


IV

(5)

Oxidation of IV with H_2O_2 gives the sulfone V.

Under more drastic conditions (at 300°), benzylidene chloride reacts smoothly with sulfur to give thianaphtheno [3, 2-b] thianaphthene (VI) [17, 21]:



VI

(6)

That compound was first prepared from S-acetylthiosalicyclic acid [22, 23], and then in approximately 1% yield from thianaphthene [24] (through a six-stage synthesis). VI was further prepared from 3-phenylthianaphthene [25].

Table 1

Reaction Products from Sulfur and Phenylchloromethanes (X)

Starting compound X	Mole ratio X : S	Reaction temperature, °C	Reaction time, hr	Reaction product	Mp, °C**	Formula	Found, %			Calculated, %			Yield, %
							C	H	S	C	H	S	
$C_6H_5CH_2Cl$	4 : 3	220—240	18	I	185	$C_{28}H_{20}S$	86.36	5.10	8.21	86.56	5.19	8.25	66.0
$C_6H_5CHCl_2$	1 : 1	220—240	8	IV*	63	$C_{14}H_9SCl$	68.61	3.57	13.31	68.70	3.71	13.10	52.1
$C_6H_5CHCl_2$	1 : 1	250—300	10	VI	214	$C_{14}H_8S_2$	69.78	3.45	26.53	69.96	3.36	26.68	61.0
$(C_6H_5)_2CHCl$	10 : 1	215	5	III	224	$C_{26}H_{20}$	94.04	6.04	—	93.97	6.03	—	69.2
$(C_6H_5)_3CCl$	1 : 1	220—230	9	IX	92	$C_{19}H_{16}$	93.45	6.84	—	93.47	6.53	—	63.2
$C_6H_5CCl_3$	1 : 1	220—240	20	No reaction									
$(C_6H_5)_2CCl_2$	1 : 1	220—240	20	No reaction									

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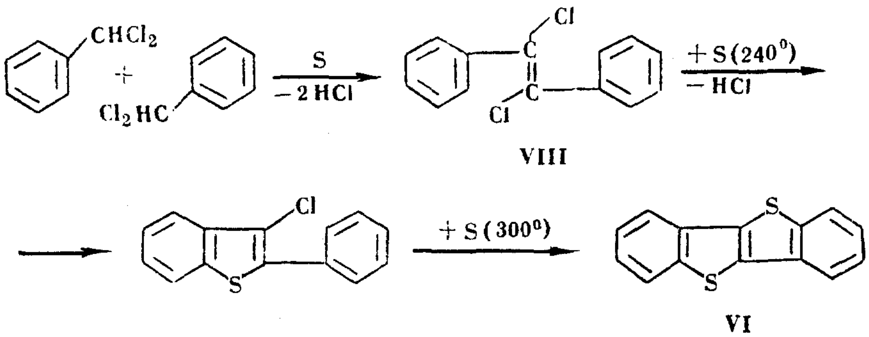
*New compound

**The literature gives mp I 185° [22], III 223° [19], IX 93° [24].

The VI isolated was oxidized with H_2O_2 to the monosulfone VII.

In general, reaction of benzylidene chloride with sulfur can be represented as follows



VIII

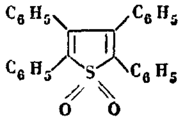
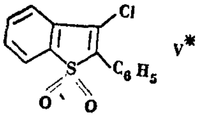
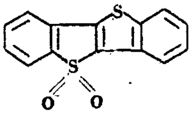
VI

(7)

However, it was not proved possible to isolate the hypothetical initial product of reaction of benzylidene chloride with sulfur 1, 2-diphenyl-1, 2-dichloroethylene (VIII). Evidently its formation is slower than its conversion to IV.

Table 2

Hydrogen Peroxide Oxidation Products (Sulfones) of the Heterocyclic Sulfur Compounds Synthesized

Starting compound	Sulfone	Mp, °C	Color of crystals	Formula	Found, %			Calculated, %			Yield, %
					C	H	S	C	H	S	
I	 II	275—277**	Bright yellow	$C_{28}H_{20}SO_2$	80.21	4.53	7.41	80.0	4.76	7.62	64.3
IV	 V*	167—168	White	$C_{14}H_9ClSO_2$	60.80	3.20	11.60	61.04	3.36	11.49	58.1
VI	 VII*	270 (decomp)	Bright yellow	$C_{14}H_8S_2O_2$	61.55	3.19	23.40	61.77	2.94	23.54	56.9

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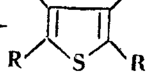
*New compound

** The literature [28] gives mp 275°.

If the reaction with sulfur is carried out with a mixture of equimolecular amounts of benzyl chloride and benzylidene chloride (with a view to preparing 2-phenylthianaphthene), the only product which can be isolated is I (65% yield)

$2RCH_2Cl + RCHCl_2 + S \longrightarrow$  $+6HCl$ (8)

$(R = C_6H_5)$ I

This indicates that elimination of HCl involving a benzene ring hydrogen atom is much more difficult than that involving side chain hydrogens.

Benzotrichloride is practically unchanged after 20 hr heating with sulfur at 225-240°. Diphenyldichloromethane behaves similarly under the same conditions. The product of reaction of sulfur with triphenylchloromethane is triphenylmethane (IX). It is known that the latter can be formed by pyrolysis of $(C_6H_5)_3CCl$ [25], but in the presence of sulfur this reaction takes place under milder conditions. It can be assumed that the reaction leading to formation of IX depends on dehydrogenation of part of the initial $(C_6H_5)_3CCl$ by free radicals $(C_6H_5)C$, which are formed by catalytic cracking by the sulfur. In the case of the most extensive dehydrogenation of (C_6H_5CCl) (to carbon), formation of IX can be represented by the equation

$$8(C_6H_5)_3CCl \xrightarrow{S} \underset{IX}{7(C_6H_5)_3CH}+19C+8HCl. \qquad (9)$$

It must be assumed, however, that dehydrogenation is less profound. Still, even for equation 9, the yield of IX from the reaction of triphenylchloromethane with sulfur is 63.2% of the theoretical.

Table 1 gives melting points, analytical data, and yields of all compounds obtained by reacting sulfur with phenylchloromethanes, and the conditions employed in their synthesis, Table 2 gives the products obtained by oxidizing the heterocyclic sulfur compounds synthesized.

Table 3

Physical Constants of the Starting Arylchloromethanes (X)

X	Bp, °C (pressure mm)	n_D^{20}	Mp, °C
$C_6H_5CH_2Cl$	178—179 (760)	1.5390	
$C_6H_5CHCl_2$	207—208 (760)	1.5502	−17
$C_6H_5CCl_3$	214 (760)	1.5584	−5
$(C_6H_5)_2CHCl$	152—153 (10)	1.5950	14
$(C_6H_5)_2CCl_2$	164—166 (12)	1.6028	
$(C_6H_5)_3CCl$			108—109
p-$ClC_6H_4CH_2Cl$	94 (10)		29
α-$ClCH_2C_{10}H_7$	148—150 (10)		

Thus reaction of sulfur with phenylchloromethanes is the simplest and most convenient method of synthesizing heterocyclic sulfur compounds of type I, IV, and VI. Further extensive synthetic possibilities of the reaction of sulfur with arylhalogenoalkanes will be described in subsequent papers.

Experimental

Starting materials

Benzyl chloride, benzal chloride, and benzotrichloride. The chemically pure products on sale were distilled through a column before use. $C_6H_5CCl_3$ was repeatedly frozen to free it from traces of $C_6H_5CHCl_2$.

Diphenylchloromethane.* A mixture of 84.1 g (0.5 mole) diphenylmethane, 33.7 g (0.25 mole) SO_2Cl_2, and 0.7 g PCl_3 was irradiated with UV light while heated at 80-90°, for 3 hr. Vacuum distillation using a column gave 28.0 g (66%) $(C_6H_5)_2CHCl$, bp 152-153° (10 mm).

Diphenyldichloromethane. A mixture of 42.1 g (0.25 mole) diphenylmethane, 101.3 g (0.75 mole) SO_2Cl_2, and 2.0 g (0.015 mole) PCl_3 was irradiated and heated, as described above, for 5 hr. Subsequent vacuum distillation through a column gave 53.5 g (90.2%) $(C_6H_5)_2CCl_2$, bp 164-167° (12 mm).

Triphenylchloromethane. A chemically pure product is on sale.

p-Chlorobenzylchloride and α-(chloromethyl) naphthalene. Prepared by chloromethylating chlorobenzene and naphthalene [26].

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

Reaction of sulfur with phenylchloromethanes.

Tetraphenylthiophene (I). A mixture of 63.3 g (0.5 mole) benzyl chloride and 9.6 g (0.3 g.at.) powdered sulfur was refluxed until the temperature reached 240° (about 15 hr), and held there for a further 3 hr. After cooling to 60°, the reaction products were stirred with 50 ml alcohol. The crystals of I which separated were filtered off with suction,

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*The diphenylchloromethane and diphenyldichloromethane were prepared by E. P. Popova.

washed with alcohol-benzene, and recrystallized from the latter mixture. Yield 27.8 g pure I (72% on the sulfur taken), mp 185°.

2-Phenyl-3-chlorothianaphthene (IV). 32.2 g (0.2 mole) benzal chloride was heated with 6.4 g (0.2 g.at.) sulfur till the boiling point of the mixture reached 240° (about 8 hr), and then for 1 hr longer. Unreacted benzal chloride (3.2 g) was distilled off under reduced pressure, and the residue extracted with 75% acetic acid. 14.3 g IV, i.e., 65% based on the reacted $C_6H_5CHCl_2$, was isolated from the extract. Recrystallization from isopropanol gave 11.5 g (52%) IV, mp 63-64°.

Thianaphtheno [3, 2-b] thianaphthene (VI). 32.2 g (0.2 mole) benzal chloride was heated with 6.4 g (0.2 g.at.) sulfur till the temperature of the reaction mixture reached 300°, then held there for 3 hr longer. After cooling and solidification, the mass was powdered and extracted with 80% CH_3CCOH. 17.3 g (72%) finely-divided crystals of VI was obtained from the extract. After recrystallizing from glacial acetic acid, the yield of pure VI (colorless crystals mp 214°) was 14.6 g, or 61%. After subliming the compound had mp 215.5°.

Tetraphenylethylene (III). 20.25 g (0.1 mole) diphenylchloromethane was heated with 0.32 g (0.01 g. at.) sulfur for 6 hr at 210-215°. The reaction products were cooled, and washed with ether. Yield of crude III mp 221° was 11.3 g (72%). Recrystallization from benzene gave 10.8 (69.2%) pure III, mp 224°.

Conversion of triphenylchloromethane into triphenylmethane (IX). 28.0 g (0.1 mole) triphenylchloromethane was heated with 3.2 g (0.1 g.at.) sulfur at 230-240° for 9 hr. After cooling the reaction mixture was extracted with acetic acid. The IX recovered from the extract was recrystallized from the same solvent. Yield 13.5 g (over 63%) pure IX, mp 92°.

Preparation of sulfones

Tetraphenylthiophene sulfone (II). 1.0 g (0.002 mole) I was heated on a water bath for 4 hr with a solution of 0.9 g (0.01 mole) 30% H_2O_2 in 45 ml glacial acetic acid. The crystalline precipitate of II which separated on cooling was recrystallized from CH_3COOH. Yield 0.7 g (64.8%) pure II, mp 275-277°.

The sulfones of V and VII were prepared similarly. The former was purified by recrystallizing from alcohol.

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