Selenium Heterocycles. XIX (1). Synthesis of Selenophenes and Triarylbenzenes from 2,5-Diaryl-1,4-dithiin 1,1,4,4-Tetroxides

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Mixtures of 2,5-diaryl-1,4-dithiin 1,1,4,4-tetroxides and selenium were subjected to heat and afforded 2,5-diarylselenophenes. Pyrolysis of 2,5-diaryl-1,4-dithiin 1,1,4,4-tetroxides led to the formation of a mixture of 1,2,4- and 1,3,5-triarylbenzenes.

In previous papers (2-5), the synthesis of 1,2,3-selenadiazoles (1) and the utility of this heterocyclic ring system for the preparation of acetylenic compounds (2) was reported. It was also demonstrated that 4-aryl-1,2,3-selenadiazoles (1) when subjected to prolonged heating, afforded 2,5-diarylselenophenes (3) and in some cases small quantities of 2,4-diarylselenophenes (4). The latter reaction was shown to be the subsequent interaction of arylacetylenes (2) with selenium which were formed during the pyrolysis. An alternative mechanism was the formation of 2,5-diaryl-1,4-diselenine (5) which would lose one selenium atom to afford (3). However (5) was found to be quite stable at the temperature of the reaction. This proves that (5) is not a precursor for (3) or (4) (See Scheme I).
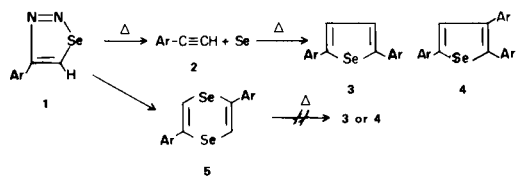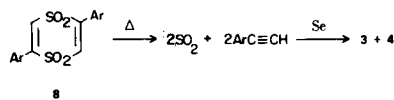

Scheme I

In connection with the above observations and keeping in mind that displacement of sulphone groups by selenium is a well known reaction in dibenzo-1,4-dithiin 1,1,4,4-tetroxide (6), giving high yields of dibenzo-1,4-diselenine (6) (selenanthrene (7)), it was decided to study the thermal reaction of selenium and 2,5-diaryl-1,4-dithiin 1,1,4,4-
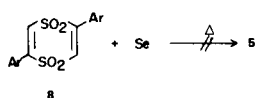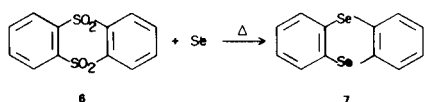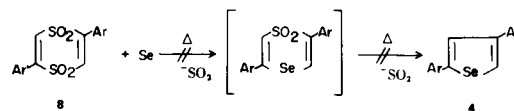

Scheme II

tetroxide (8). However, the reaction product was not the expected 5, but 3 as a major product along with small quantities of 4 (See Schemes II and III).

On the basis of these observations it was assumed that in the presence of selenium, during pyrolysis, 8 was completely decomposed to the corresponding arylacetylene and sulphur dioxide. At this stage selenium existed in the medium reacted with the arylacetylene to give 3 and 4. This pathway was supported by the detection of arylacetylene at the beginning of pyrolysis as well as by comparison of thermal reaction of arylacetylene and selenium giving 3 and 4 (7) (See Scheme III).

Scheme III

An alternative mechanism would be the replacement of one sulphone group of 8 by selenium followed by elimination of the second sulphone group. A similar ring contraction reaction has been reported in the case of 2,5-diphenyl-1,4-dithiin 1,1-dioxide, giving 2,5-diphenylthiophene (sulphur analogue of 4) through pyrolysis (8). This mechanism should lead to the formation of 4 as major product. However, 4 was found only in trace amount (See Scheme IV).

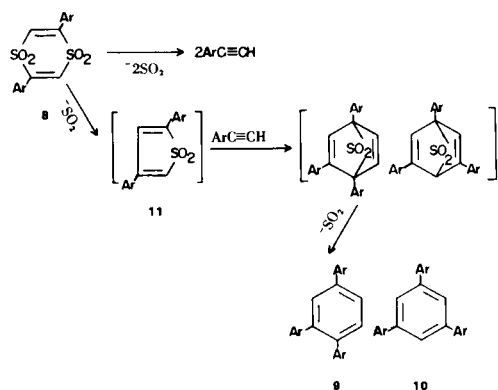

Scheme IV

The possibility of interconversion of 3 and 4 by heat was studied and it was proved that prolonged heating of each isomer did not result in isomerisation. It was interesting to observe that in keeping with the pyrolysis results, frag-

mentation pattern in the mass spectra of **8** was in accordance with the formation of the arylacetylene. In all cases the base peak corresponded to acetylenic ion.

For further elucidation of the mechanism of the reaction of **8** and selenium, it was necessary to study the behaviour of **8** towards heat. Heating the pure tetroxide **8** to its melting point gave a vigorous decomposition reaction and sulphur dioxide was evolved. Arylacetylene which was identified in each case, was rapidly disappeared and the reaction product was found to be a mixture of 1,2,4-triarylbenzene (**9**) and 1,3,5-triarylbenzene (**10**). Separation of the mixture of two isomers was done in the case of triphenylbenzene by glc method. A possible mechanism for the formation of **9** and **10** is shown in Scheme V.

Scheme V

Although, the examination of the reaction mixture revealed that no 2,5-diarylthiophene 1,1-dioxide (**11**) was present. However, it could be envisaged that the latter compound was formed by the elimination of one sulphone group from the starting tetroxide which then interacts with arylacetylene (this was formed from decomposition of a part of the tetroxide) giving **9** and **10**. Ours and others (9) failure to prepare 2,5-diarylthiophene 1,1-dioxide (**11**) is in agreement with the above postulate. This is supported

by the fact that 2,3,4,5-tetraphenylthiophene 1,1-dioxide reacts with phenylacetylene to give pentaphenylbenzene; (10) also thiophene 1,1-dioxide has been reported to undergo Diels-Alder reaction in dilute solution. However the dioxide could not be isolated, because it polymerised rapidly (11). It is noteworthy to mention that the careful examination of the thermal reaction product of tetroxide **8** and selenium, by glc method, revealed that only trace amounts of **9** and **10** were formed. It is therefore concluded that in the presence of selenium the formation of selenophene is a faster process.

All compound prepared are summarized in Tables I, II, and III.

EXPERIMENTAL

Melting points were taken on a Kofler hot stage microscope and uncorrected. The uv spectra were obtained using a Varian Techtron 635 spectrophotometer. The ir spectra were recorded on a Leitz model III spectrograph. The nmr were taken on a Varian A60A instrument. Mass spectra were recorded on a Varian Mat 111 spectrometer. Glc was conducted on a Varian Aerograph 900 instrument using a 4% SE-30 on chromosorb w column (10 ft x 0.25 in). Thermal reaction were conducted on a metalic bath heating 10° above the melting point of the parent tetroxide.

1,4-Dithiins.

The dithiins used in this work were prepared by the methods described in the literature (12,13). New 1,4-dithiins prepared are summarized in Table I.

2,5-Di-p-fluorophenyl-1,4-dithiin 1,1,4,4-Tetroxide (**8b**).

To a boiling solution of 2,5-di-p-fluorophenyl-1,4-dithiin (306 mg.) in acetic acid (20 ml.), 30% hydrogen peroxide (20 ml.) was added portionwise during one hour; the clear solution was refluxed for 6 hours. After cooling, the crystalline precipitate was separated and recrystallized from acetic acid to give (82 mg., 22%) of white crystals, m.p. 269-270°. Molecular weight by mass spectroscopy m/e 368 with base peak at m/e 120; ν max (potassium bromide): 1618, 1530, 1337, 1251, 1176, 1134, 865, 839, and 825 cm^{-1}.

All 2,5-diaryl-1,4-dithiin 1,1,4,4-tetroxides prepared are summarized in Table II.

Table I

Ar	R	M.p. (°C)	Yield %	Formula	Analysis (a)	
					C	H
P-FC$_6$H$_4$	H	164-165	20	C$_{16}$H$_{10}$F$_2$S$_2$	63.16	3.29
					63.22	3.03
2-Naphthyl	H	212-215	50	C$_{24}$H$_{16}$S$_2$	78.26	4.35
					78.18	4.29
C$_6$H$_5$	CH$_3$	123	21	C$_{18}$H$_{16}$S$_2$	72.97	5.41
					73.03	5.44

(a) Top row, calculated; bottom row, found.

Table II
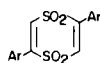
						Analysis (a)	
Compound	Ar	M.p. (°C)	Yield %	Uv Max (ε)	Formula	C	H
8a	C_6H_5	232 (b)	30	276 (14562)	$C_{16}H_{12}O_4S_2$	57.83	3.61
						57.71	3.66
8b	p-FC_6H_4	269	22	278 (8209)	$C_{16}H_{10}F_2O_4S_2$	52.17	2.71
						52.25	2.80
8c	p-ClC_6H_4	263	56	280 (6716)	$C_{16}H_{10}Cl_2O_4S_2$	47.88	2.49
						47.83	2.53
8d	p-BrC_6H_4	270	32	283 (4617)	$C_{16}H_{10}Br_2O_4S_2$	39.18	2.04
						39.25	2.08
8e	p-2-Naphthyl	309	21	208 (12825)	$C_{24}H_{16}O_4S_2$	66.66	3.70
						66.60	3.80

(a) Top row, calculated; bottom row, found. (b) H. H. Szmant, and J. Dixone, *J. Am. Chem. Soc.*, 75, 4354 (1953); m.p. 232°.

Table III
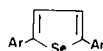
					Analysis (a)	
Compound	Ar	M.p. (°C)	Yield %	Formula	C	H
3a	C_6H_5	171-172 (b)	48	$C_{16}H_{12}Se$	67.74	4.23
					67.91	4.22
3b	p-FC_6H_4	189-191 (c)	51	$C_{16}H_{10}F_2Se$	60.18	3.13
					60.11	3.15
3c	p-ClC_6H_4	186-187 (d)	68	$C_{16}H_{10}Cl_2Se$	54.57	2.83
					54.31	2.80
3d	p-BrC_6H_4	215-216 (e)	59	$C_{16}H_{10}Br_2Se$	43.57	2.26
					43.60	2.33
3e	2-Naphthyl	218-220	50	$C_{24}H_{16}Se$	75.20	4.17
					75.31	4.11

(a) Top row, calculated; bottom row, found. (b) Lit (6) 170-172°. (c) Lit (6) 188-191°. (d) Lit (6) 185-188°. (e) Lit (6) 214-216°.

Oxidation of 2,5-dimethyl-3,6-diphenyl-1,4-dithiin as well as 2,3,5,6-tetraphenyl-1,4-dithiin (14) afforded banzoic acid rather than desired tetroxides.

Reaction of 2,5-Diphenyl-1,4-dithiin 1,1,4,4-tetroxide (8a) with Selenium.

A mixture of 2,5-diphenyl-1,4-dithiin 1,1,4,4-tetroxide (332 mg., 1 mmole) and powdered black selenium (80 mg.) was heated for 15 minutes on a metalic bath at 240°. The reaction mixture was cooled and extracted with chloroform and chromatographed on a short column containing silica gel with layers of activated charcoal. After evaporation of the solvent, the residue was recrystallized from aqueous ethanol to give 2,5-diphenylselenophene (3) (135 mg., 84%), m.p. 171-172°. Uv, ir, and mass spectra of the compound obtained was superimpossible with those of the authentic

sample (7). Concentration of the mother liquor gave a residue, which was recrystallized from aqueous ethanol to give 2,4-diphenyl-selenophene (16 mg., 5%), m.p. and mixed m.p. were identical with that of an authentic sample (7,15).

Pyrolysis of 2,5-Diphenyl-1,4-dithiin 1,1,4,4-Tetroxide (8a). Preparation of 1,2,4- and 1,3,5-Triphenylbenzenes (9 and 10).

2,5-Diphenyl-1,4-dithiin 1,1,4,4-tetroxide (8a), (500 mg.) was heated under reflux on a metalic bath at 240°: A vigorous decomposition reaction occurred and phenylacetylene started to reflux (a sample was taken and subjected to ir, nmr., and mass spectroscopy for identification purposes). After about 15 minutes no more phenylacetylene was present. At this stage the reaction mixture was dissolved in chloroform and subjected to preparative tlc on alumina using chloroform-petroleum ether (50:50) as running

solvent. After evaporation of the solvent the residue (258 mg., 56%) was subjected to preparative glc and found to consist of (60%) 1,2,4- and (40%) 1,3,5-triphenylbenzenes. The structure were assigned by comparison with authentic samples.

Similar results were obtained from the other tetroxides without separating the isomers, and the elemental analysis were as expected.

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