Selenium Heterocycles. XXIX (1). Reaction of Substituted 2-Thioxo-1,3-thiaselenoles with Ethyl Diazoacetate, Ethyl Azidoformate and Phenyl Azide

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Reaction of 5-substituted 2-thioxo-1,3-thiaselenoles with ethyl diazoacetate, phenyl azide and ethyl azidoformate afforded 2-substituted ω-carbethoxy-1,4-thiaselenafulvenes (II), 5-substituted 2-phenylimino-1,3-thiaselenoles (IV) and 5-substituted 2-carbethoxyimino-1,3-thiaselenoles (V), respectively. The structure of these compounds were confirmed by spectroscopic methods and chemical analysis.

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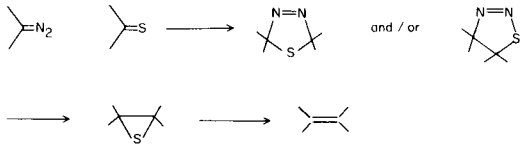
In continuation of the study on the chemistry of selenium heterocyclic compounds (2-7), and as a part of a program designed to expand the chemistry of 2-thioxo-1,3-thiaselenole (8) we have studied the reaction of the latter with organic azides and ethyl diazoacetate.

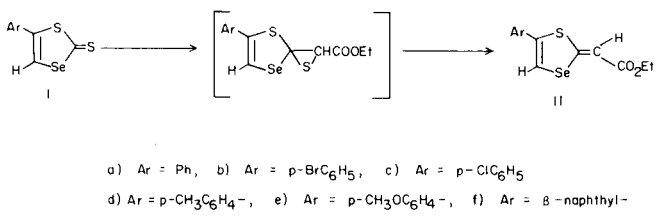
The reaction of diazo alkanes with thioketones has been extensively studied and is useful for olefin synthesis. The intermediate episulfides were isolated, and recently the unstable initial adducts, Δ^3-1,3,4- and / or Δ^2-1,2,3-thiadiazolines, have been isolated (9,10).



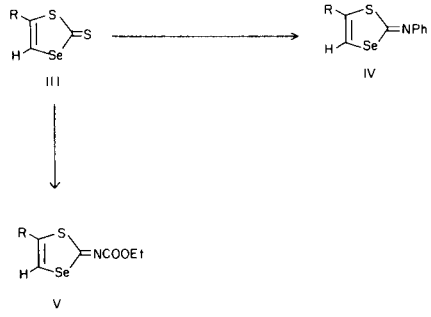
The reaction of α-diazo esters with thiocarbonyls is considered to proceed similarly, and the α,β-unsaturated carbonyl compounds were obtained (11).

We have recently reported a general procedure for the preparation of 5-substituted 2-thioxo-1,3-thiaselenoles (I) (8), we now report the reaction of I with ethyl diazoacetate, phenyl azide and ethyl azidoformate. The reaction of I with ethyl diazoacetate proceeded smoothly and afforded 2,ω-disubstituted 1,4-thiaselenafulvenes (II) (Scheme I).

Scheme I



a) Ar = Ph, b) Ar = p-BrC_6H_5, c) Ar = p-ClC_6H_5
d) Ar = p-$CH_3C_6H_4$-, e) Ar = p-$CH_3OC_6H_4$-, f) Ar = β-naphthyl-



a) R = CH_3, b) R = $(CH_3)_2CH$-, c) R = t-butyl, d) R = C_6H_5
e) R = p-ClC_6H_4-, f) R = p-$CH_3C_6H_4$-, g) R = p-$CH_3OC_6H_4$-
h) R = β-naphthyl

The structure of the compound II was confirmed by spectroscopic methods (ir, nmr and ms) and chemical analysis. In the nmr spectrum Hω appeared as a doublet (J = 1.4 Hz) at about 6.50 Hz. The coupling constant is in accordance with *trans* stereochemistry for the fulvene (see reference 3). The nmr spectral data are summarized in Table II.

Recently, the reaction of some heterocyclic thiones with ethyl azidoformate has been reported (12). The reaction of phenyl azide with compound III afforded 5-substituted 2-phenylimino-1,3-thiaselenoles (IV) in moderate yield. We have also studied the reaction of ethyl azidoformate with compound I. In this case 2-carbethoxyimino-1,3-thiaselenoles (V) were isolated. The ir spectra of the latter showed absorptions around 1650 cm^{-1} for the ester function.

This absorption is in accordance with the suggested structure. In the nmr spectrum the H_4 appeared from 7.12 to 7.70 Hz. The similar value is reported for 5-substituted 1,3-thiaselenole moiety (8). The nmr spectral data are summarized in Table I.

The physical constants of the compounds prepared are summarized in Table II.

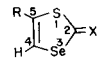
EXPERIMENTAL

Melting points were taken on a Kofler hot stage microscope and were uncorrected. The ir spectra were obtained on a Perkin Elmer Model 267

0022-152X/80/010117-03$02.25

Table I

Spectral Data of Derivatives of 1,3-Thiaselenoles



Compounds No.	R	X	^{1}H-Nmr (Deuteriochloroform): δ (ppm) Hω	H4	aryl	alkyl	ir (cm^{-1})
IIa	Ph-	C(COOEt)H	6.50 (d, 1H, $J_{4,\omega}$ = 1.2 Hz)	7.30 (d, 1H, $J_{4,\omega}$ = 1.2 Hz)	7.66-7.33 (m, 5H)		1655
IIb	*p*-Br-C_6H_4-	"	6.50 (d, 1H, $J_{4,\omega}$ = 1.4 Hz)	7.30 (d, 1H, $J_{4,\omega}$ = 1.4 Hz)	7.38 (q, 4H)		
IIc	*p*-Cl-C_6H_4-	"	6.45 (d, 1H, $J_{4,\omega}$ = 1.4 Hz)	7.30 (d, 1H, $J_{4,\omega}$ = 1.4 Hz)	7.33 (s, 4H)		1655
IId	*p*-CH_3-C_6H_4-	"	6.50 (d, 1H, $J_{4,\omega}$ = 1.4 Hz)	7.56-7.06 (m, 5H, H_4 and aromatic)		2.38 (s, 3H, $CH_3C_6H_4$)	1660
IIe	*p*-$CH_3OC_6H_4$-	"	6.50 (d, 1H, $J_{4,\omega}$ = 1.4 Hz)	7.20 (d, 1H, $J_{4,\omega}$ = 1.4 Hz)	7.40 (d, 2H), 6.90 (d, 2H)		1660
IIf	β-naphthyl	"	6.53 (d, 1H, $J_{4,\omega}$ = 1.4 Hz)	8.0-7.36 (m, 5H, H_4 and aromatic)			1660
Va	CH_3	N-CO_2Et		7.16 (q, 1H, J = 1.5 Hz)		2.40 (d, 3H, J = 1.5 Hz)	1660
Vb	$(CH_3)_2CH$	"		7.20 (d, 1H, J = 1 Hz)		1.30 (q, 6H)	1663
Vc	*t*-Bu-	"		7.16 (s, 1H)		1.36 (s, 9H)	1660
Vd	Ph-	"		7.70 (s, 1H)	7.66-7.30 (m, 5H)		1650
Ve	*p*-Cl-C_6H_4-	"		7.70 (s, 1H)	7.43 (s, 4H)		1660
Vf	*p*-$CH_3C_6H_4$-	"		7.60 (s, 1H)	7.28 (q, 4H)		1660
Vg	*p*-$CH_3OC_6H_4$-	"		7.63 (s, 1H)	7.50 (d, 2H)		1650
					6.97 (d, 2H)		
Vh	β-naphthyl	"					1650
IVa	CH_3	N-C_6H_5		6.53 (q, J = 0.5 Hz)	7.67-6.87 (m, 5H)	2.17 (d, 3H, J = 0.5 Hz)	
IVb	$(CH_3)_2CH$	"		6.50 (d, 1H, H_4, J = 0.8 Hz	7.40-6.67 (m, 5H, aromatic)	1.23 (q, 6H, CH_3, J = 7 Hz)	
IVc	*t*-Bu-	N-C_6H_5		6.63 (s, 1H, H_4) (a)	7.60-6.93 (m, 5H, aromatic)	1.33 (s, 9H, CH_3)	

(a) In compounds IVd to IVh H_4 appeared in aromatic region (7.0-8.0).

Table II

R	X	M.p. °C (a)	Yield	Formula	C% Calcd.	C% Found	H% Calcd.	H% Found	N% Calcd.	N% Found
Ph-	C(H)COOEt	145-147	30	$C_{13}H_{12}O_2SSe$	50.16	49.91	3.86	3.99		
p-Br-C_6H_4-	"	149-151	30	$C_{13}H_{11}BrO_2SSe$	40.00	40.18	2.82	2.64		
p-Cl-C_6H_4-	"	140-141	35	$C_{13}H_{11}ClO_2SSe$	45.15	45.01	3.18	3.04		
p-MeC_6H_4-	"	174-177	40	$C_{14}H_{14}O_2SSe$	51.69	51.87	4.31	4.50		
p-CH_3-OC_6H_4-	"	158-160	30	$C_{14}H_{14}O_3SSe$	49.27	49.48	4.11	4.32		
β-naphthyl	"	153-155	35	$C_{17}H_{14}O_2SSe$	56.51	56.30	3.88	4.11		
CH_3-	N-Ph	66-67 (b)	25	$C_{10}H_9NSSe$	47.24	47.01	3.54	3.37	5.51	5.70
$(CH_3)_2CH$-	"	59-60 (b)	40	$C_{12}H_{13}NSSe$	51.06	50.89	4.61	4.45	4.96	4.83
t-Bu-	"	50-52 (b)	45	$C_{13}H_{15}NSSe$	52.70	52.98	5.07	5.18	4.73	4.92
Ph	"	116-117 (b)	45	$C_{15}H_{11}NSSe$	56.96	56.78	3.48	3.63	4.43	4.61
p-Cl-C_6H_5-	"	145-146	35	$C_{15}H_{10}ClNSSe$	51.36	51.55	2.86	2.99	3.99	3.78
p-MeC_6H_4	"	124-125	40	$C_{16}H_{13}NSSe$	58.18	58.36	3.94	3.81	4.24	4.06
p-$MeOC_6H_4$-	"	131-132	40	$C_{16}H_{13}NOSSe$	55.49	55.28	3.76	3.53	4.05	4.26
β-naphthyl	"	181-182 (c)	25	$C_{19}H_{13}NSSe$	62.30	62.48	3.55	3.74	3.83	3.99
CH_3	N-CO_2Et	103-104 (d)	30	$C_7H_9NO_2SSe$	33.60	33.79	3.60	3.81	5.60	5.78
$(CH_3)_2CH$-	"	72-73	30	$C_9H_{13}NO_2SSe$	38.85	39.12	4.68	4.46	5.04	5.23
t-Bu-	"	67-68 (b)	40	$C_{10}H_{15}NO_2SSe$	41.10	40.95	5.14	5.35	4.79	4.58
Ph-	"	143-144	40	$C_{12}H_{11}NO_2SSe$	46.15	46.01	3.53	3.71	4.49	4.68
p-Cl-C_6H_4-	"	171-172	35	$C_{12}H_{10}ClNO_2SSe$	41.56	41.78	2.89	2.65	4.04	4.26
p-MeC_6H_4-	"	154-155	45	$C_{13}H_{13}NO_2SSe$	47.85	47.63	3.99	4.15	4.29	4.44
p-$MeOC_6H_4$-	"	166-167	35	$C_{13}H_{13}NO_3SSe$	45.61	45.83	3.80	3.61	4.09	4.28
β-naphthyl-	"	193-194	40	$C_{16}H_{13}NO_2SSe$	53.04	53.23	3.59	3.78	3.87	3.64

(a) Unless otherwise mentioned the compound was crystallized from ether. (b) This compound was crystallized from petroleum ether. (c) This compound was crystallized from acetone. (d) This compound was crystallized from carbon tetrachloride.

spectrograph. Nmr spectra were determined using a Varian T-60 spectrometer and chemical shifts (δ) are in ppm relative to internal tetramethylsilane. Mass spectra were run on a Varian MAT-311 spectrometer at 70 ev.

Reaction of Ethyl Diazoacetate with 5-Phenyl-2-thioxo-1,3-thiaselenole (Ia).

A solution of 5-phenyl-2-thioxo-1,3-thiaselenole (Ia, 2.58 g., 0.01 mole) (8) and 2 ml. of ethyl diazoacetate in xylene (50 ml.) was refluxed for 5 hours. Ethyl diazoacetate (2 ml.) was added again and refluxing was continued for 5 hours. The solvent was evaporated and the residue was crystallized from chloroform to give 1 g. of the starting material (Ia). The mother liquor was evaporated and the residue was column chromatographed (silica gel). The column was eluted consecutively with petroleum ether and 10% chloroform-petroleum ether. Fractions of 300 ml. each were collected; each fraction was monitored by thin layer chromatography on silica gel with chloroform-petroleum ether (1:1) as the solvent.

The starting material was eluted at first (500 mg.) and then the desired compound, 2-phenyl-ω-carbethoxy-1,4-thiaselenafulvene (II) was crystallized from ether (0.39 g., 30%), m.p. 145-147°; ir (potassium bromide): 1655 cm^{-1}; nmr (deuteriochloroform): 7.66-7.33 (m, 5H, aromatic), 7.30 (d, 1H, H_4, $J_{4,\omega}$ = 1.2 Hz), 6.50 (d, 1H, Hω, $J_{4,\omega}$ = 1.2 Hz), 4.30 (q, 2H, OCH_2) and 1.33 ppm (t, 3H, CH_3); ms: m/e (%), 312 (84), 310 (41), 267 (35), 240 (88), 238 (49), 182 (28), 137 (23), 102 (100), 76 (21) and 51 (21).

Anal. Calcd. for $C_{13}H_{12}O_2SSe$: C, 50.16; H, 3.86. Found: C, 49.91; H, 3.99.

Other 2-aryl-ω-carbethoxy-1,4-thiaselenafulvenes (IIb-IIf) were prepared similarly.

Reaction of Phenyl Azide with 5-Isopropyl-2-thioxo-1,3-thiaselenole.

A solution of 5-isopropyl-2-thioxo-1,3-thiaselenole (IIIb, 2.23 g., 0.01 mole) and phenyl azide (2 ml.) in xylene was refluxed for 4 hours. Phenyl azide (2 ml.) was again added and refluxing continued for 10 hours. The solvent was evaporated and the residue was purified by column chromatography as explained above. The product was crystallized from petroleum ether to give 1.27 g. (45%) of 5-isopropyl-2-phenylimino-1,3-thiaselenole (IVb), m.p. 59-60°; nmr (deuteriochloroform): 7.40-6.67 (m, 5H, aromatic), 6.50 (d, 1H, H_4, J = 0.8 Hz), 2.73 (m, 1H, CH) and 1.23 ppm (q, 6H, CH_3, J = 7 Hz); ms: m/e (%), 283 (83), 281 (21), 185 (61), 180 (36), 165 (43), 156 (60), 99 (22), 92 (71), 77 (43) and 67 (31).

Anal. Calcd. for $C_{12}H_{13}NSSe$: C, 51.06; H, 4.61; N, 4.96. Found: C, 50.89; H, 4.45; N, 4.83.

Other 5-substituted 2-phenylimino-1,3-thiaselenoles (IVa, IVc-IVh) were prepared similarly.

Reaction of Ethyl Azidoformate with 5-Methyl-2-thioxo-1,3-thiaselenole (IIIa).

A solution of 5-methyl-2-thioxo-1,3-thiaselenole (IIIa, 1.95 g., 0.01 mole) and 2 ml. of ethyl azidoformate in carbon tetrachloride (50 ml.) was refluxed overnight. Ethyl azidoformate (2 ml.) was again added and refluxing was continued for 24 hours. The solvent was evaporated and the residue was purified by column chromatography as explained above. The starting material was crystallized from petroleum ether (1 g.) and the product was crystallized from carbon tetrachloride to give 0.37 g. (30%) of 5-methyl-2-carbethoxyimino-1,3-thiaselenole (Va), m.p. 103-104°; ir (potassium bromide): 1660 cm^{-1}; nmr (deuteriochloroform): 7.16 (q, 1H, H_4, J = 1.5 Hz), 4.30 (q, 2H, OCH_2), 2.40 (d, 3H, CH_3, J = 1.5 Hz) and 1.37 ppm (t, 3H, CH_3); ms: m/e (%), 251 (23), 152 (55), 151 (29), 150 (26), 149 (22), 89 (19), 59 (23), 39 (42) and 29 (100).

Anal. Calcd. for $C_7H_9NO_2SSe$: C, 33.60; H, 3.60; N, 5.60. Found: C, 33.79; H, 3.81; N, 5.78.

Other 5-substituted 2-carbethoxyimino-1,3-thiaselenoles (Vb-Vh) were prepared similarly.

Acknowledgment.

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REFERENCES AND NOTES

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For part XXVIII see A. Shafiee, A. Mazloumi and V. I. Cohen, "Selenium Heterocycles XXVIII, Synthesis of pyrrolo[3,2-*d*]selenazole and pyrrolo[3,2-*d*]thiazole. Two novel Heterocycles.", *J. Heterocyclic Chem.*, **16**, 1563 (1979).

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