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PHOTOCHEMISTRY OF ORGANIC SELENIUM AND TELLURIUM COMPOUNDS [1]

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Timely reviews marking the spectacular rise of organoselenium chemistry (1,2,3) in modern organic synthesis have been published recently. Neither these papers (1,2,3) nor recent books (4,5,6) about organochalcogen compounds include special chapters dealing with photoreactions of organic selenium or tellurium compounds.

This is the first review on the photochemistry of organic derivatives of selenium or tellurium.

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[1] Dedicated to Prof. Dr. phil. A. Schönberg on the occasion of his 87th birthday.

Photodecomposition and formation of the elemental chalcogens is frequently cited as a nuisance factor in the preparation and storage of organic selenium and tellurium compounds. However, this behavior is not universal, and many stable compounds of these elements are known and well documented (4,5,6). It appears then rather remarkable that the literature to date contains little structure / property information and very limited details on these grossly observable photoeffects.

This review covers the literature up to spring 1979.

1. Selenols. Tellurols

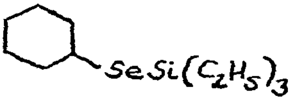
The photoinduced addition of selenols 1 to alkenes 2 was first investigated by Russian chemists in 1969. They obtained selenides 3 in up to 90 % yield (7):

$$\underset{1}{(C_2H_5)_3M\text{-}SeH} + \underset{2}{CH_2{=}CHR} \xrightarrow{h\nu} \underset{3}{(C_2H_5)_3M\text{-}Se(CH_2)_2R}$$

$$\left(\begin{array}{l} R = Ph,\ COOC_2H_5,\ CN \\ M = Si,\ Ge \end{array}\right)$$

In the reaction of germanium compound 1 with methyl acrylate, $[Ge(C_2H_5)_3]_2Se$ (4) was formed in 32 % yield, as a byproduct (7). The same selenide 4 was formed when the germanium compound 1 was reacted with acrylonitrile, giving $(NCCH_2CH_2)_2Se$ in 53 % yield.

Hexene was irradiated in the presence of triethylsilylhydroselenide 1 to give the normal addition product 5 in 72 % yield (7).



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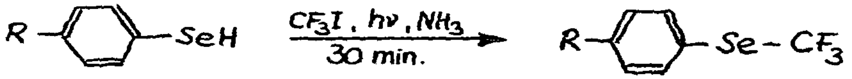
Trifluoromethyl iodide reacted with selenophenols 6 under irradiation to give the perfluoralkylated selenides 7 (8)



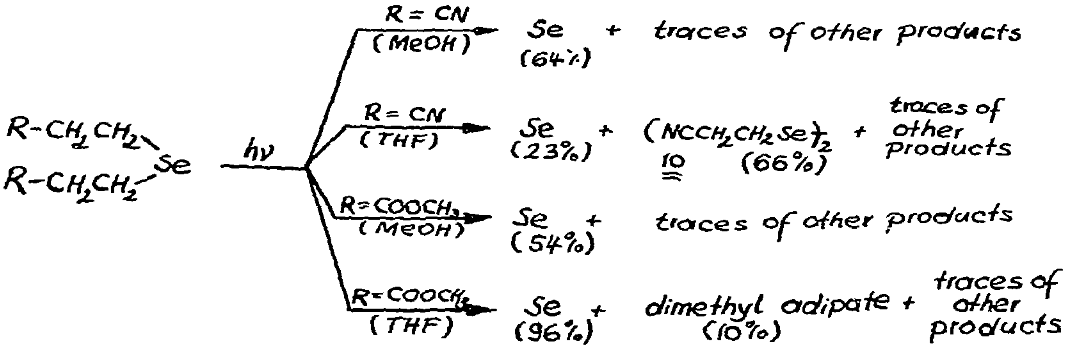
6 7

$R = H\ (69\ \%),\ CH_3\ (83\ \%),\ CF_3\ (74\ \%),\ Br\ (34\ \%)$

Related reactions have been observed between the phenylselenide (9) or phenyltelluride (10) anion and haloarenes. They were reported to undergo photo S_{RN1} reactionsupon irradiation in liquid ammonia.

2. Selenides, Tellurides

The photolysis of bis(2-cyanoethyl)selenide (8) and bis [2-(methoxycarbonyl)-ethyl] selenide (9) was reported to give a complex mixture of products (11). The reaction was strongly solvent-dependent. In methanol solution, 8 gave 64 % elemental selenium and traces of hydrogen selenide and acrylonitrile. In tetrahydrofuran solution, less selenium was obtained. The major product was the diselenide 10

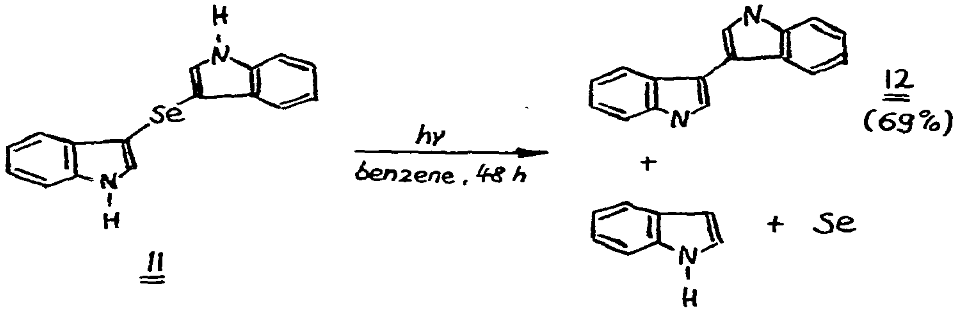


$R = CN$ 8

$R = COOCH_3$ 9

The photolysis of bis 2-(methoxycarbonyl)ethyl selenide (2) (11) in methanol solution gave a result similar to that obtained for the nitrile 1 except for the formation of a trace of dimethyl adipate. In tetrahydrofuran solution, the latter was obtained in 10 % yield, together with an essentially quantitativeyield of selenium (11).

It is interesting that the photolysis of diindolyl selenide (11) gave biindolyl (12) in a fairly clean reaction (12).



Indole and elemental selenium were also observed upon irradiation, but no yield was given (12).

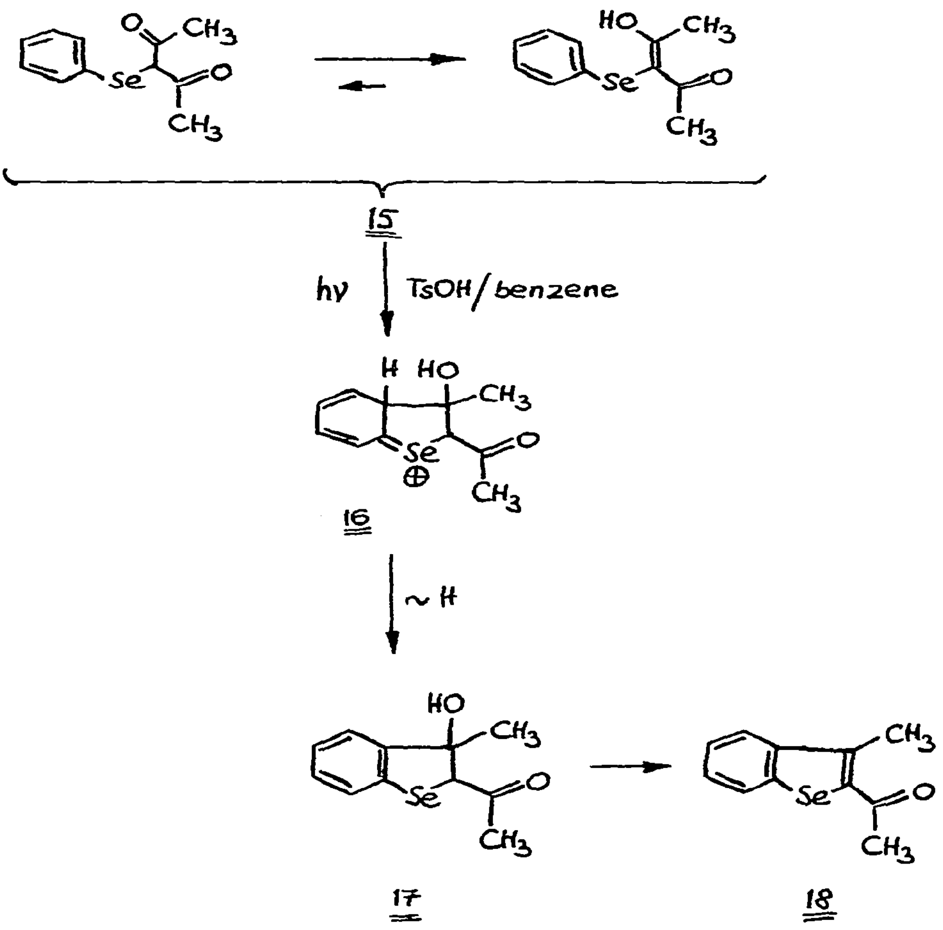
The pulse radiolysis of Ar_2Se and Ar_2Te (Ar = 4-methoxyphenyl) in neutral and acidic methanolic solution permitted the observation of transient assigned to the radicals ArSe$^\bullet$ and ArTe$^\bullet$ (13).

The elimination of elemental chalcogen is known to occur when dimethyl telluride (13) is irradiated (14,15). The UV photolysis of 13 is a usable source of ground state (^{3}P 2,1,0) tellurium atoms which may react with olefins to form π complexes (11). These cyclic adducts have only transient existence and were prepared for kinetic measurements (15).

The photochemical oxidation of dibenzyl telluride (16) (14) in CCl_4 afforded benzaldehyde (42 %), benzyl alcohol (24 %), toluene (4 %), and 1,2-diphenylethane (5 %) after 24 hrs of irradiation. In another experiment using a low concentration of 14 and excess pure oxygen, only benzaldehyde (66 %) and benzyl alcohol were detected. In both experiments black elemental tellurium was produced.

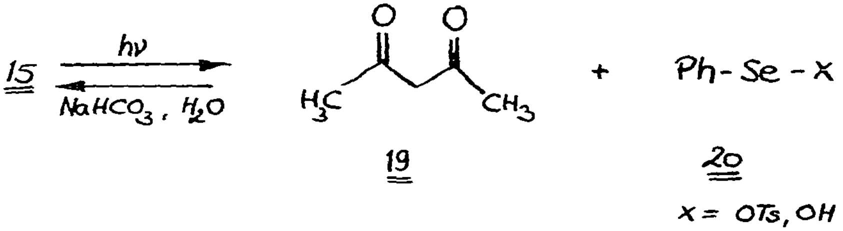
The literature also includes descriptions of photoreactions for selenides and tellurides which do not deposit elemental chalcogenes. upon irradiation. Therefore, although the elimination of elemental selenium (11,12) and tellurium (14,15) is an important reaction pathway, it is not a general rule.

Preparative-scale Pyrex-filtered irradiation of the organoselenide 15 in benzene solution saturated with p-toluenesulfonic acid at $\sim$15°C while purging with argon gave 2-acetyl-3-methylbenzo [b] - selenophene (16) in 60 % isolated yield (17). Due to the high yield, analogous photoreactions may be useful for synthesis of a variety of aryl-fused selenophenes:



The mechanism of the interesting transformation 15 ⟶ 18 presumably involves photocyclization of 15 to selenocarbonyl ylide 16, which undergoes rearrangement to β-hydroxy ketone 17 followed by acid-catalyzed elimination of the elements of water to give benzoselenophene 18 (17). That 17 actually is an intermediate in the conversion of 15 ⟶ 18 was demonstrated (17) by photolysis of 15 in benzene-d_6 containing acetic acid (1 equiv) in a degassed NMR tube. Extended irradiation led to a mixture of products (vide supra), a major component (~30 %) of which gave NMR singlets at δ1.92 (3 protons), 2.31 (3 protons), and 4.86 (1 proton) and has been assigned structure 17 on the basis of chemical reactivity. Thus, treatment of the photolysis mixture with a catalytic amount of p-toluene-sulfonic acid resulted in rapid disappearance of the three NMR singlets attributable to 17 together with an enhancement of absorptions due to the methyl resonances of benzoselenophene 18 (δ 2.60 and 2.73) (17).

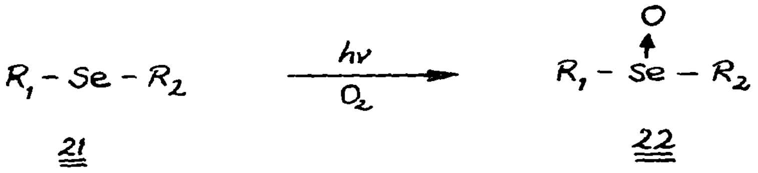
The photochemistry of 15 also includes cleavage of carbon-selenium bonds (17): NMR analysis of products of a brief irradiation revealed that 15 (19 %), benzoselenophene 18 (54 %) and acetylacetone 19 (27 %) were present. Treatment of the crude photoproducts with aqueous sodium bicarbonate solution resulted in the disappearece of 19 with concomitant formation of selenide 15. The latter must undergo carbon-selenium bond cleavage to generate acetylacetone (19) and PhSeX (20); on treatment with base, 15 is regenerated from 19 and 20 (17).



Formation of considerable ammounts of acetylacetone (19) occured when 15 was photolysed in benzene-acetic acid solution, while in pure benzene, photocleavage was the predominant reaction.

Dialkyl as well as aryl alkyl selenides 21 were oxidized to form selenoxides 22 under irradiation (18) in methanol solution in the presence of rose bengal and oxygen.

The chemical yield may be up to 95 %:



	R_1	R_2	yield [%]	recovered 21 [%]
a	Ph	CH_3	95	-
b	Ph	CH_2Ph	70	10
c	Ph	C_3H_7 - CHOH - CH(C_3H_7)	28	45
d	CH_3	C_9H_{19} - CH(CH_3)	85	10
e	CH_3	C_3H_7 - CHOH - CH(C_3H_7)	70	15

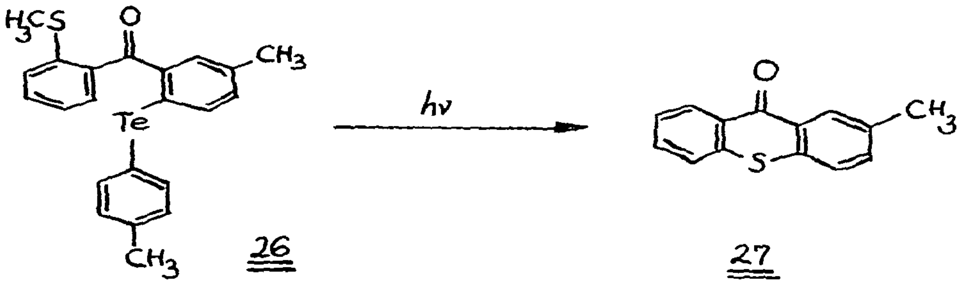
The oxidation of selenides 21 to selenoxides 22 with photochemically generated singlet oxygen (18) was described recently. In the case of the selenides 21c and 21e 5-octene-4-ol was formed in 15 and 27 % yield, resp., in addition to selenoxides 22c and 22e.

A general method for the preparation of perfluoralkyl- and mixed alkyl perfluoroalkyl tellurides under very mild conditions was described by DENNISTON and MARTIN (19). By condensing dimethyltelluride 13 in a Vycor tube and subjecting the system to UV light, the authors obtained, with good conversion of the iodide, the perfluoroalkyl substituted tellurides 24 and 25 (19).

$$\underset{23a,b}{R_fJ} + \underset{13}{CH_3-Te-CH_3} \xrightarrow[20\,h]{h\nu} \underset{24a,b}{R_fTeCH_3} + \underset{25a,b}{R_fTeR_f}$$

$$\left(\begin{array}{lll} a & R_f = & CF_3 \\ b & & C_2H_5 \end{array}\right)$$

In a new type of photosubstitution, telluride 26 was reported to form the thioxanthone 27 via a cyclization reaction (20,21).



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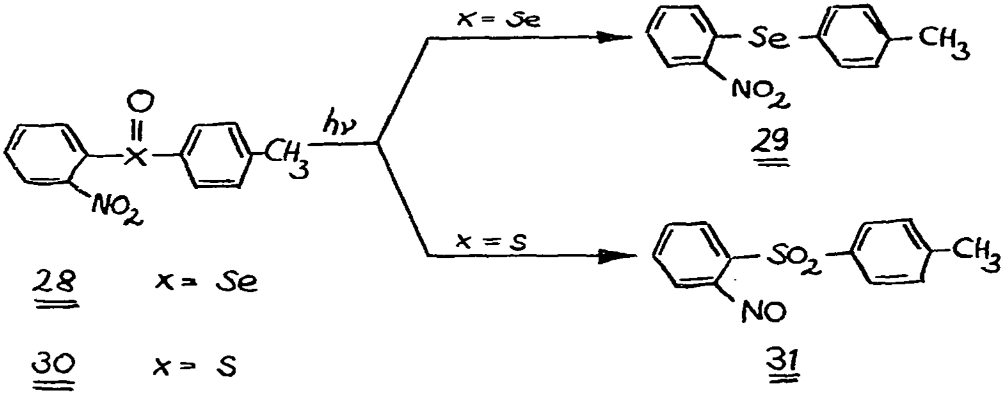
3. Selenoxides

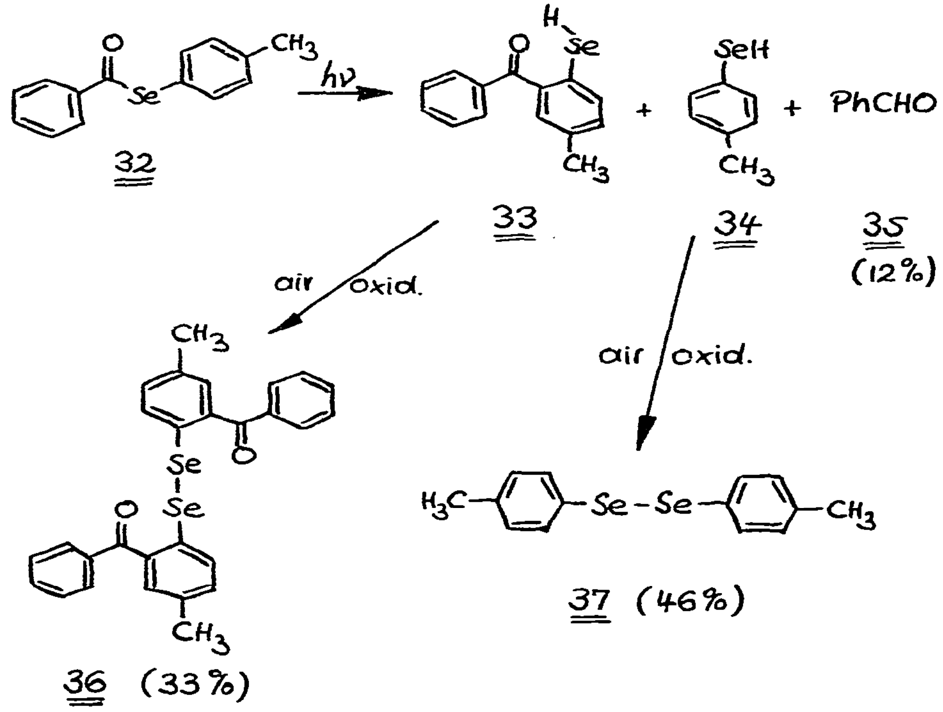
A solution of 4-methyl-2'-nitro-diphenyl selenoxide (28) in benzene was observed to give the deoxigenation product 4-methyl-2'-nitro-diphenyl selenide (29) on irradiation (22). In contrast to this result irradiation of the analogous sulfoxide 30 gave the sulfone 31 (23).

It has recently been reported that sulfides undergo photooxidation to form sulfoxides if the former are irradiated in the presence of selenoxides (24) in an argon atmosphere (24).

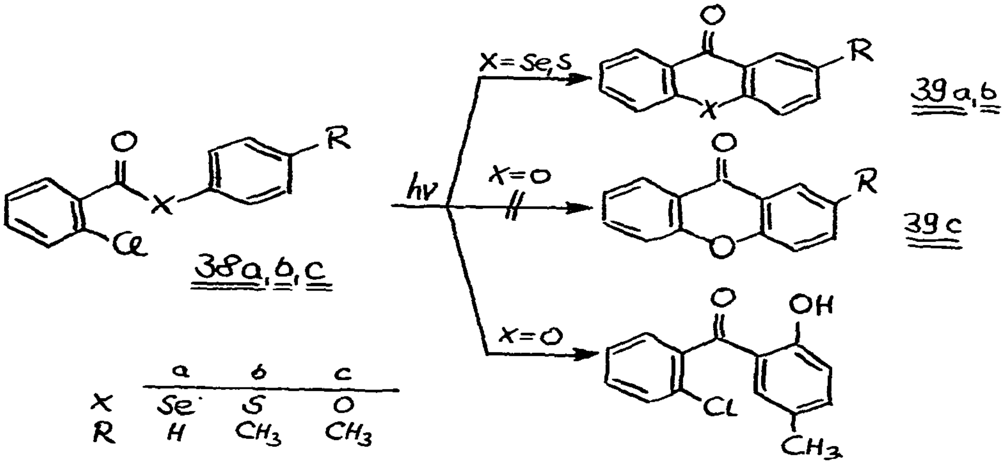


4. Selenol esters, Tellurol esters

The first report of photoreactions of Se-aryl carboselenoates was published in 1976 (25). Se-(4-methylphenyl)selenobenzoate (32)was reported to give the seleno-photo-Fries product 33a, selenocresol (34), and benzaldehyde (35) on irradiation of a benzene solution with UV light (25). The sensitive selenoles 33a and 34 were detectable by NMR-Spectroscopy of the crude degassed reaction mixture (26), and separated from each other by chromatography. The products formed the isolable deselenides 36 and 37 in 33 % and 46 % yield, resp., on oxidation with air:

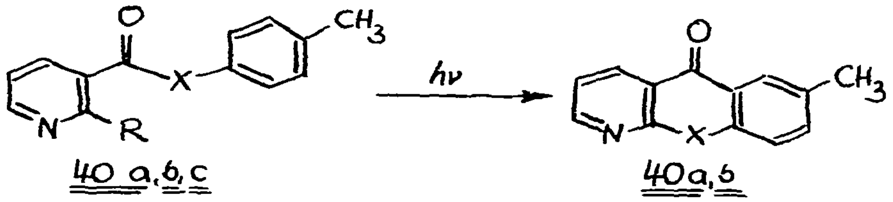


Irradiation of Se-phenyl-2-chloro-selenobenzoate (38a) with UV light gave the expected selenoxanthone (39a) in 19 % yield (25).



	a	b	c
X	Se	S	O
R	H	CH_3	CH_3

The new heterocycle 5 H- 1 benzoselenino 2,3-b pyridine (41a) was prepared by the related photorearrangement of the seleno nicotinoate 40a in 25 % yield (27):



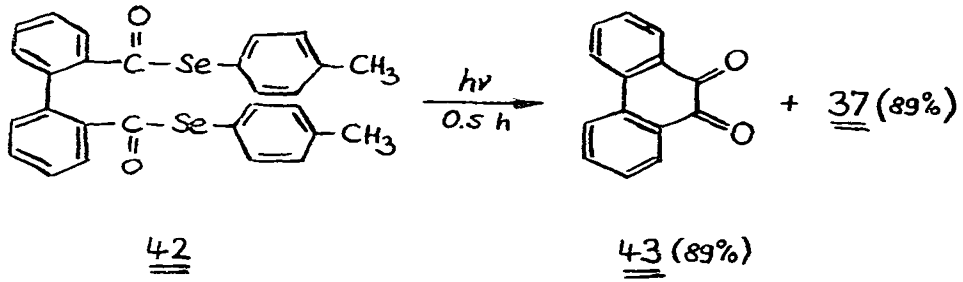
	a	b	c
x	Se	Se	S
R	Cl		Cl

The synthesis of the pharmaceutically interesting heterocycle 41a via an intramolecular photo-Friedel-Crafts-reaction was described recently (85). Starting from 2-(4-methylphenylseleno)-selenonicotinate 40b the pyridin derivative 41a was obtained in 67 % yield (87) upon irradiation.

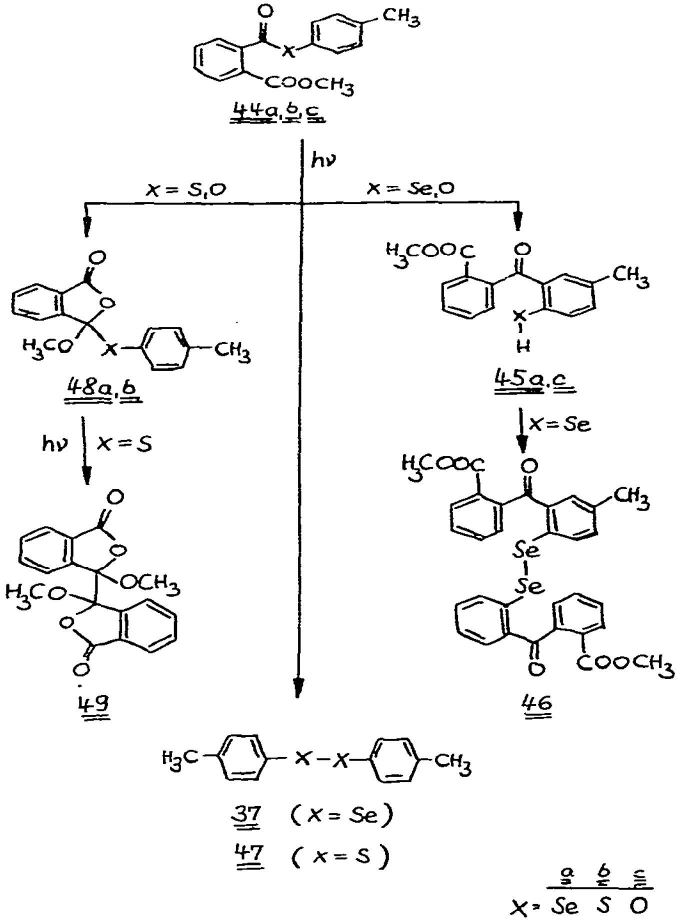
Analogous photoreactions are known for ortho acceptor substituted thiol esters to give thioxanthones (28 - 30).

The formation of xanthones from photolysis of arylesters such as 38c has never been reported.

The dieselenol ester 42 furnishes in a surprisingly neat photoreaction both phenanthraquinone (43) and the diselenide 37 in good yield (25):



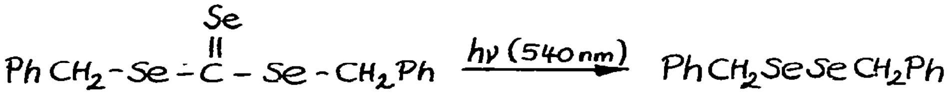
Phenanthraquinone (43) was recently reported (31,32) to be a photoproduct of some di-S esters of 2,2-dithiodiphenic acid. Thus parallelism is observed in photoreactions of these thiol esters and the selenol esters 42. Seleno-photo-Fries products, as observed in the conversion 32 $\longrightarrow$ 33, were also obtained upon irradiation of selenol ester 44a (33):



The photochemistry of selenol ester 44a is of interest because of neighbouring group participtaion which is known to give phthalide (48b and 48c, resp.). Secondary photoproducts (34,35) 49 were obtained from the UV irradiation of the isosteric thiol ester 44b (33,36). The isoelectronic methyl(4-methyl-phenyl)-diphthalate 44c furnishes the hydrobenzophenone 45c upon irradiation, along with phthalide 48c.

In spite of photoproducts 45a and 45c, parallelism is observed in the photochemical behavior of selenol ester 44a and ester 44c. Surprisingly the selenol esters exhibit a photochemical behavior inbetween that of the isoelectronic oxygen esters (photo-Fries reaction furnishes hydroxybenzophenones and phenols, but usually no aldehyde (37)) and the corresponding thiol esters (aldehyde formation, no photo-Fries reaction (38)).

The triselenocarbonate 50 is reported to undergo photolysis by irradiation at 540 nm to give dibenzyl diselenide in a good yield (39):

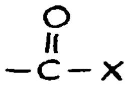


$$PhCH_2{-}Se{-}\overset{\overset{\large Se}{\|}}{C}{-}Se{-}CH_2Ph \xrightarrow{h\nu\,(540\,nm)} PhCH_2SeSeCH_2Ph$$

50

When the photolysis of 50 is carried out at 350 nm in benzene the reaction is complicated by the formation of secondary photolysis products of the dibenzyl diselenide. Thus at 350 nm the major products are benzaldehyde and selenium (39).

In general, parallelism is observed in the photochemistry of the selenol esters 32, 38a, 40a, 42, and 44a and compounds containing the structural element



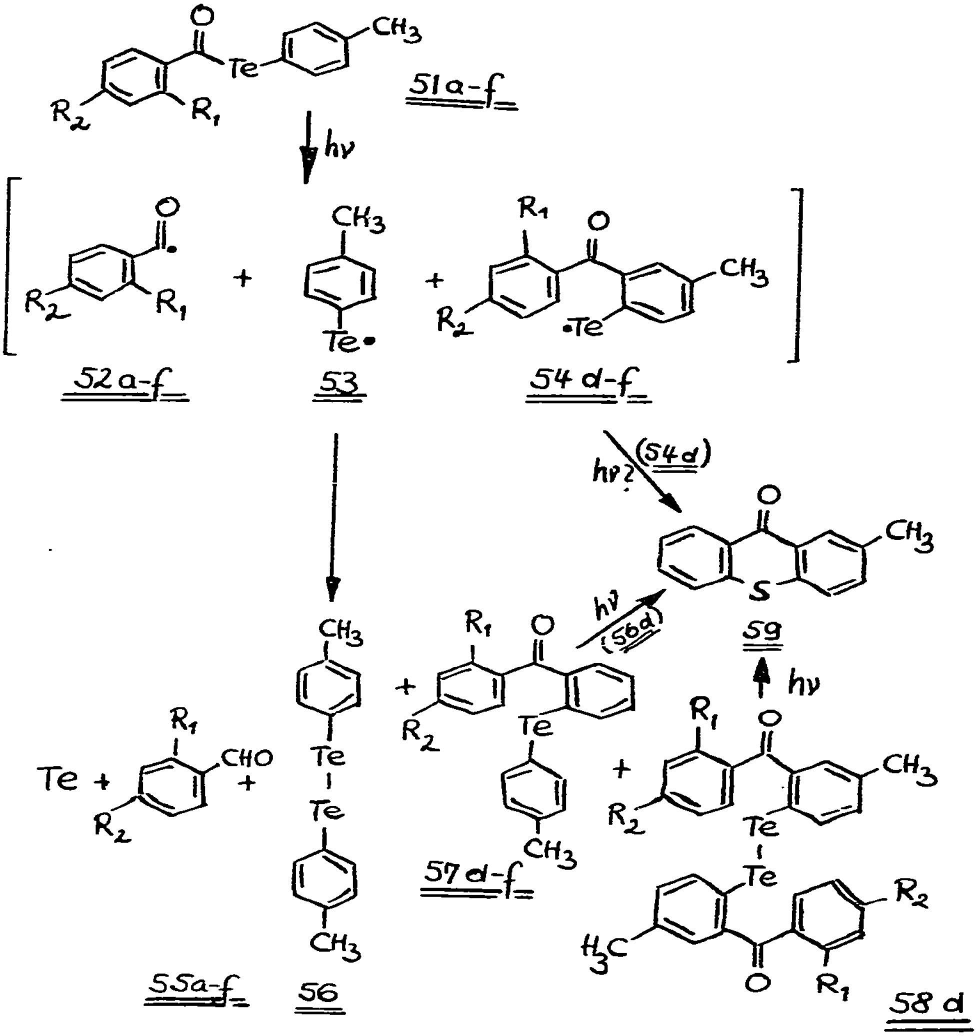
$$-\overset{\overset{O}{\|}}{C}-X$$

(X = NH-aryl 32), O-aryl 32), or S-aryl 23-25, 33))

In all cases the acyl-X bond undergoes photolysis.

The photoproducts of the triselenocarbonate 50 are also derived from α-cleavage reactions.

The first report of photoreactions of telluroesters was published very recently (20). Telluroesters 51 a - f undergo photoinduced α-cleavage to give a variety of products, including elemental tellurium, ditellurides, aldehydes, and photo-Fries products (20,21):



	R_1	R_2	yields (%)					
			Te	55a-f	56	57d-f	58d	59
a	H	H	30	22	46			
b	H	OCH_3	+ a)	15	62			
c	Cl	H	19	9	49			
d	SCH_3	H	25	13	33	2	11	22
e	SO_2CH_3	H	11	6	26	10		
f	OCH_3	H	24	21	26	6		

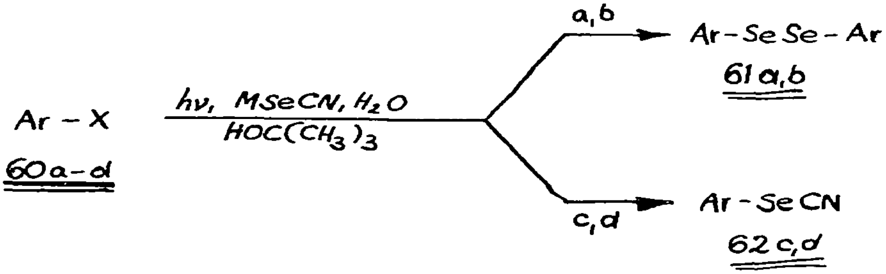
a) no yield given

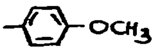
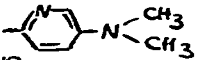
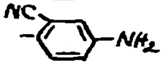
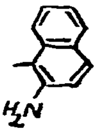
Cleavage of the carbonyl-tellurium bond under ultraviolet irradiation led to free aroyl radicals 52 a - f, and telluryl radical 53. The aroyl radicals abstracted hydrogen to give the benzaldehydes 55 a - f. The telluryl radical dimerized to form the ditelluride 56. In the case of the ortho-O and ortho-S substituted tellurol esters 51 d - f, the benzophenones 57 d - f were formed as secondary products of a initial telluro-photo-Fries reaction (21). In the special case of the tellurol ester 51 d six photoproducts have been isolated:

elemental tellurium, aldehyde 55d, ditelluride 56, benzophenone 57d, ditelluride 58, and thioxanthone 59 (20,21). Independently, it was shown that 57d and 58d are suitable substrates to form thioxanthone 59 on ultraviolet irradiation (20,21).

5. Selenocyanates, Tellurocyanates

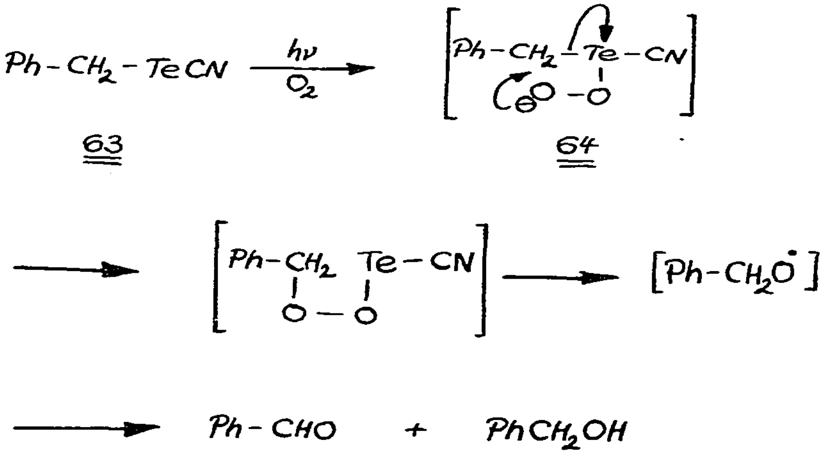
Diaryl diselenides 61 or arylselenocyanates 62 were the main products of the photoinduced substitution reaction of halogen atoms by selenocyanate ions in the aromatic compounds 60 (40).



	M	X	Ar
a	Na	Cl	
b	K	Br	
c	K	Cl	
d	K	Cl	

The most obvious reaction of benzyl tellurocyanate (63) was very recently reported (41) to be its darkening when exposed to light and air. 63 was surprisingly stable to light alone in the absence of oxygen. Thus a solution of 63 in $CDCl_2$ could be irradiated under nitrogen for 40 hr without decomposition (41). Under similar conditions, but under an oxygen atmosphere, a black solid (elemental tellurium) precipitated, while the solution contained only a mixture of benzaldehyde (60 %) and benyl alcohol (40 %) (41).

The mechanism of this first and only photooxydation of a tellurocyanate reported in the literature may involve attack by singlet oxygen to give the 1,3-dipolar peroxide 64. Rearrangement of 64 may give an unstable benzyl peroxytellurocyanate 65, from which benzaldehyde and benzyl alcohol are derivable by way of benzyloxy radicals (41).



6. Selenonium Compounds, Diorganotellurium dichloride

The ability of triphenylselenonium fluoborate (66a) to undergo a photochemical reaction with triphenylphosphine was demonstrated in 1974 (42).

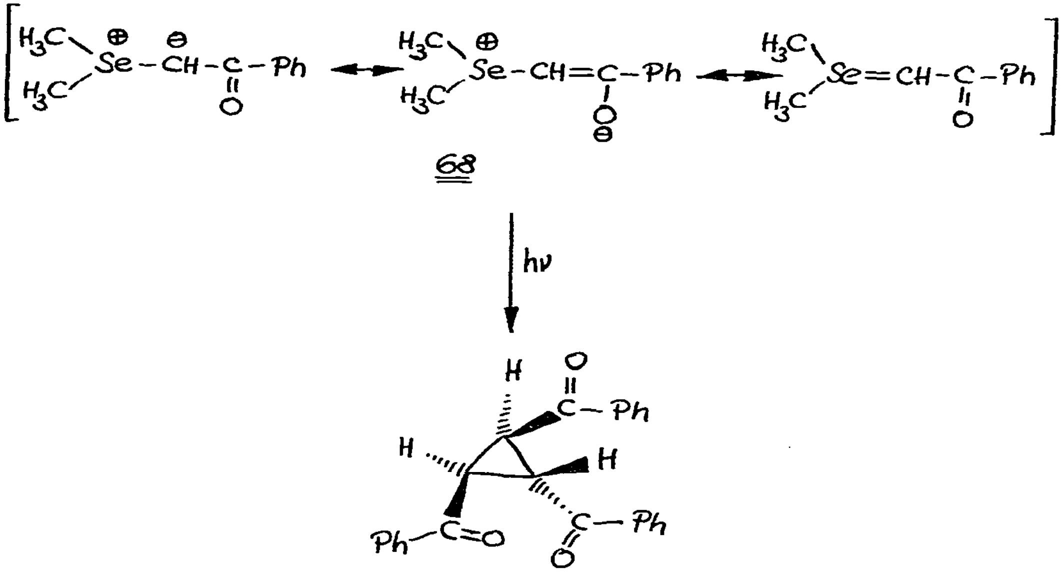
$$(Ph)_3X^{\oplus}(BF_4)^{\ominus} + (Ph)_3P \xrightarrow{h\nu} (Ph)_4P^{\oplus}(BF_4)^{\ominus} + Ph{-}X{-}Ph$$

66a,b 67

	X	yield 67(%)
a	Se	85
b	S	84

The same result was observed in the case of the sulfonium compound 66b. Although the mechanism of the investigated photoreaction (42) of the selenonium salt with triphenylphosphine was not given special attention, it is possible that it is analogous with the known mechanism (43) for the reaction between diaryliodonium salts and triphenylphosphine.

The ylide was observed to undergo phototrimerisation (44) with elimination of dimethyl selenide to give tribenzoylcyclopropane 69:



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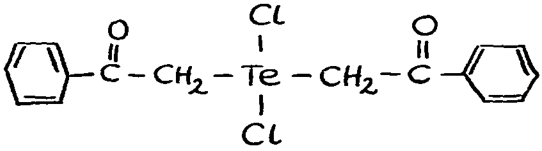
Selenonium salts may be of practical importance as photo initiators (86).

The photochemical ß-cleavage and Norrish type II reaction for bis(benzoylmethyl)tellurium dichloride (70) have been investigated (45)



70

Photolysis of 70 with 313 nm light in degassed liquid solutions resulted in the formation of acetophenone, chloroacetophenone, and tellurium metal as the principal photoproducts (45). In H-atom donating solvents, the quantum yield of acetophenone produced may exceed 2, while chloroacetophenone was formed only in trace amounts. In inert solvents, chloroacetophenone and tellurium were formed in major amounts with lesser amounts of acetophenone and trace amounts of dibenzoylethane also produced (45).

7. Diselenides, Ditellurides

Some studies have been made on photochemical reactions of diselenides. The ultraviolet irradiation of dibenzyl diselenide (71) is well documented (39,46 - 55) and, in the absence of oxygen, leads to dibenzyl selenide 72 and selenium (39,46 - 52):

$$\underset{\underline{\underline{71}}}{\mathrm{Ph{-}CH_2{-}Se{-}Se{-}CH_2{-}Ph}} \xrightarrow[\text{oxygen excluded}]{h\nu} \mathrm{Se} + \underset{\underline{\underline{72}}}{\mathrm{PhCH_2SeCH_2Ph}}$$

The reaction route involves initial photochemical cleavage of the Se-C bond. Any cleavage of the Se-Se bond simply reverses (40).

$$\underset{\underline{\underline{71}}}{\mathrm{(PhCH_2)_2Se_2}} \xrightarrow{h\nu} \mathrm{PhCH_2Se_2^{\bullet}} + \mathrm{Ph\dot{C}H_2}$$

$$\mathrm{PhCH_2\dot{S}e_2} \longrightarrow \mathrm{PhCH_2\dot{S}e} + \mathrm{Se}$$

$$\mathrm{Ph\dot{C}H_2} + \underset{\underline{\underline{71}}}{\mathrm{(PhCH_2)_2Se_2}} \longrightarrow \underset{\underline{\underline{72}}}{\mathrm{(PhCH_2)_2Se}} + \mathrm{PhCH_2\dot{S}e}$$

$$\mathrm{Ph\overset{\circ}{C}H_2} + \mathrm{PhCH_2\dot{S}e} \longrightarrow \mathrm{(PhCH_2)_2Se}$$

$$\mathrm{PhCH_2\dot{S}e} \longrightarrow \mathrm{(PhCH_2)_2Se_2}$$

An ESR study on ultraviolet-irradiated diphenyl diselenide by Schmidt et al. (56) indicated the formation of phenylselenyl and phenylselenoselenyl radicals. Both S-S and C-S cleavage have been shown to be important processes for photolysis of dibenzyl disulfide (56 - 58). Therefore, it is reasonable to propose that both Se-Se and C-Se scissions are possible in the photolysis of 71. Initially-formed benzylselenyl radicals may combine or attack the weak Se-Se linkage leading to radical displacement and reformation of 71. Neither of these reactions lead to the observed photoproducts. Therefore, the most probable step leading to the formation of the observed photolysis products is the C-Se scission (46).

When a $CDCl_3$ solution of the diselenide 71 was irradiated in the presence of oxygen the products were benzaldehyde (42 %), benzyl alcohol (24 %), toluene (4 %), 1,2-diphenylethane (5 %) and elemental selenium (53). The irradiation of 71 at 350 nm in the presence of air is reported (39) to give elemental selenium in 93 % yield and benzaldehyde (50 - 63 %).

The first photochemical deselenation of a diselenide by a tertiary phosphine was described by Cross and Millington (59). More detailed results on this interesting photoreaction were recently published by the same group (55). Irradiation of the diselenide 71 in the presence of an excess of triphenylphosphine (48) in degassed acetonitrile at 350 nm yielded 66.1 % dibenzyl selenide 72, 32.3 % bibenzyl and 65.1 % of triphenylphosphine selenide (73):

$$\underset{71}{PhCH_2SeSeCH_2Ph} + (Ph)_3P \xrightarrow[\text{excluding air}]{h\nu} \underset{72}{PhCH_2SeCH_2Ph} + (CH_2Ph)_2 + \underset{73}{(Ph)_3PSe}$$

Under these conditions, the formation of elemental selenium was completely suppressed (48). In the presence of molecular oxygen 73 reacted further to produce triphenyl phosphine oxide and elemental selenium (48).

The major primary photoprocess in the conversion 71 72 + 73 is the facile Se-Se bond cleavage. It appears, that benzylselenyl radicals are trapped by triphenyl phosphine to form triphenylselenide 73 and benzyl radicals, which subsequently react to form bibenzyl and dibenzyl selenide (72) (48):

$$\underset{\mathbf{71}}{PhCH_2SeSeCH_2Ph} \xrightarrow{h\nu} 2\ PhCH_2\dot{Se}$$

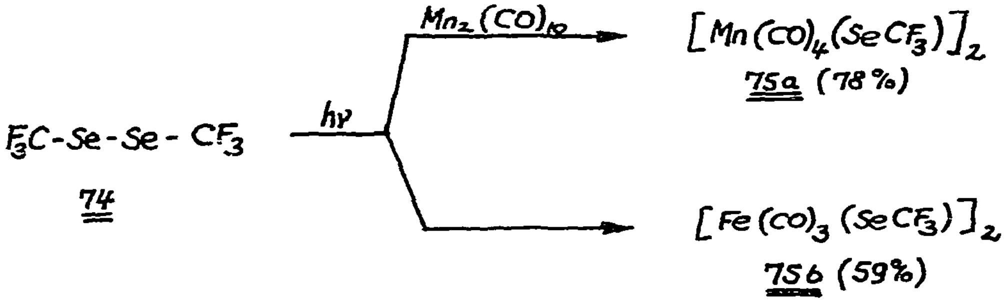
$$PhCH_2\dot{Se} + (Ph)_3P \longrightarrow Ph\dot{C}H_2 + \underset{\mathbf{73}}{Ph_3PSe}$$

$$Ph\dot{C}H_2 + PhCH_2SeSeCH_2Ph \longrightarrow \underset{\mathbf{72}}{PhCH_2SeCH_2Ph} + PhCH_2\dot{Se}$$

$$2\ Ph\dot{C}H_2 \longrightarrow PhCH_2CH_2Ph$$

The reactions of several other diselenides and tertiary phosphines under UV irradiation were examined. They proceeded smoothly to give phosphorus (V) selenides and diorganyl monoselenides (52,55 59). Closely related reactions are the photochemically initiated chain reactions between organic disulfides and tertiary phosphines to give phosphorus(V) sulfides (60,61).

Bis(trifluoromethyl) diselenide (74) produced CF_3Se radicals under UV irradiation, and reacted with metal carbonyl radicals $M(CO)_n$ (M = Mn, n = 5, M = Fe, n = 4) to give ultimately $M(CO)_{n-1}(SeCF_3)_2$ (75) (62):



Diazomethane was reported (63) to react with diselenides 76 under sunlight to furnish diselenoacetals 77:

$$\underset{\underline{76a,b}}{R\text{-}Se\text{-}Se\text{-}R} + CH_2N_2 \xrightarrow{\text{sunlight}} \underset{\underline{77a,b}}{R\text{-}Se\text{-}CH_2\text{-}Se\text{-}R} + N_2$$

	a	b
R	Ph	CH_2 Ph
yield 77	quantitative	quantitative

Ditellurides reacted similary with diazomethane but did not require sunlight (63).

Very few studies have been made on photochemical reactions of diorganoditellurides. The first report on the photochemistry of ditellurides was published by Spencer and Cava (16) in 1977. Dibenzyl ditelluride (78) was reported to be very sensitive to UV light and produces in the presence of oxygen the same photoproducts obtained from dibenzyl diselenide (71) (16) under identical reaction conditions, except tellurium instead of selenium:

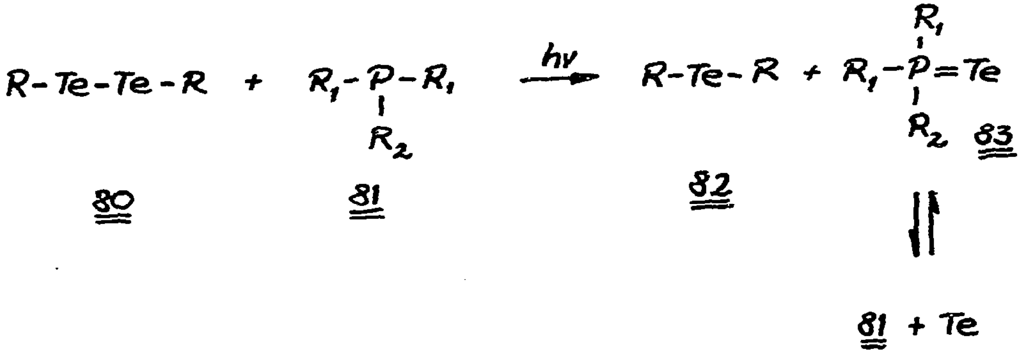
$$PhCH_2TeTeCH_2Ph \xrightarrow[O_2]{h\nu} \underset{(42\%)}{PhCHO} + \underset{(21\%)}{PhCH_2OH} + \underset{(21\%)}{PhCH_3} + \underset{(7\%)}{PhCH_2CH_2Ph} + Te$$

In the absence of oxygen parallelism is also observed in the photochemical behaviour of the ditelluride 78 (16) and the isoelectronic diselenide 71 (46). The ditelluride 78 gave the telluride 79 and elemental tellurium under irradiation (16,64):

$$\underset{\underline{78}}{PhCH_2TeTeCH_2Ph} \xrightarrow[N_2]{h\nu} \underset{\underline{79}\ (\text{quant.})}{PhCH_2TeCH_2Ph} + \underset{(\text{quant.})}{Te}$$

When diorganoditellurides 80 were photolysed in the presence of triorganylphosphines (81), monotellurides 82 and tellurium metal were again produced (64). Tellurium was deposited only in some cases

(64), in others it was reported to form triorganyl phosphine tellurides (65) (83), which are known (64,66) to be unstable and rapidly equilibrates to triorganophosphine 81 and elemental tellurium.



The ditelluride 58d (20,21) was reported to undergo an unexpected photosubstitution to yield the thioxanthone 59 (see chapter: selenol and tellurol esters).

Pulse radiolysis experiments of diarylditellurides have been described recently (13) and permitted the observation of ArTe• radicals.

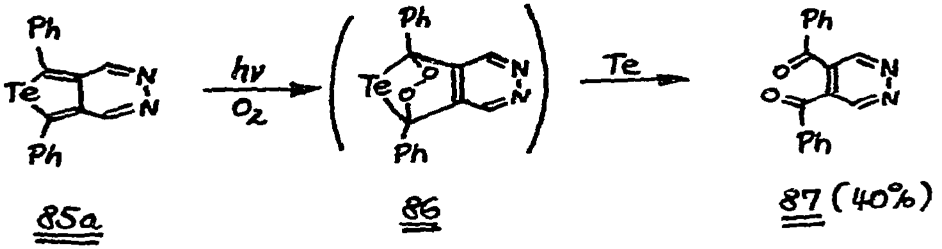
8. Heterocyclic Compounds containing either Se or Te

There is a very little information in the literature concerning the photochemistry of heterocyclic compounds containing either Se or Te in the ring.

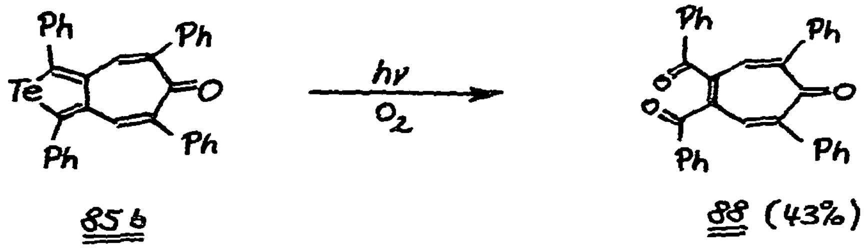
While investigating heterocyclopentadiene photochemistry, Barton and Nelson (67) irradiated 2,5-diphenyltellurophene (84). They observed no photoproducts and recovery of the starting material 84 was quantitative.

84

The aromatic character of the tellurophene ring system was confirmed and exemplified by inability to act as a diene in a Diels-Alder reaction, even under forcing conditions (67). This result may be interpreted to be in contrast with that described in the paper of Winter and coworkers (68). The authors (68) reported that the tellurophenes 85a and 85b

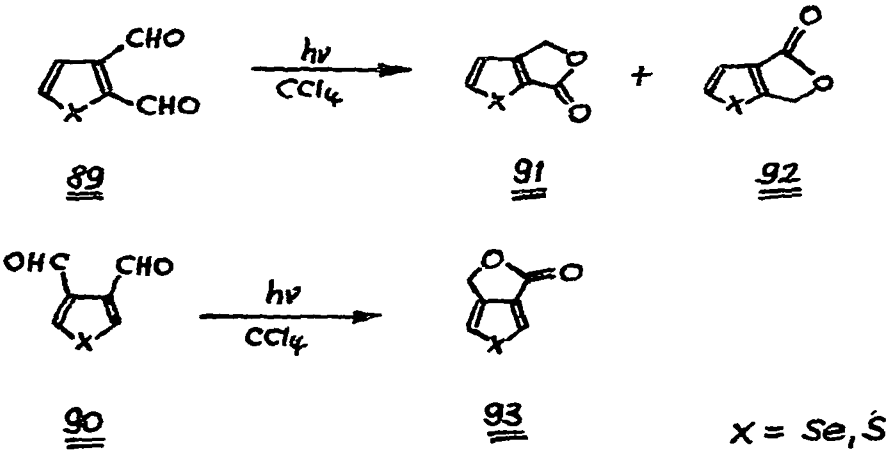


are decomposed under the influence of light and oxygen to form 4,5-dibenzoylpyridazine (87) and 4,5-dibenzoyl-2,7-diphenyl-2,4,6-cycloheptatriel-1-one (88), *resp.* (68).

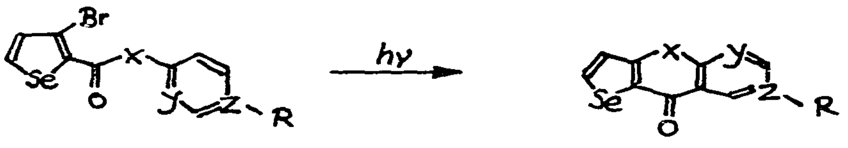


The mechanism for the transformation 85a ⟶ 87 presumably involves the singlet oxygen Diels-Alder adduct 86. Similar adducts are known to be formed from singlet oxygen reacting with other heterocyclopentadienes (69,70).

Diformyl selenophenes (71) 89 and 90 (x = Se) underwent photocyclization of the side chain, forming the lactones 91 - 93 in good yields. The same reaction is reported (71) for the isoelectronic thiophenes 89 and 90 (X = S):

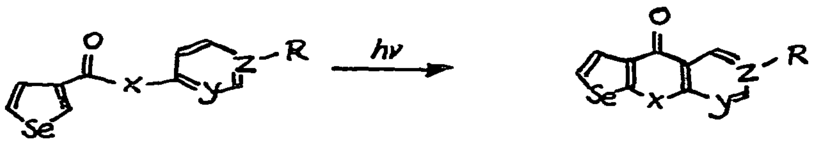


The new heterocyclic compounds 95 a - h were recently reported (72,73) to be photoproducts of the selenophenes 94 a - h. The mechanism of the intramolecular photoreaction of the 3-bromoselenophenes 94 a - d (72) may be analogous to the mechanism described for related seleno- (25) and thio- (28,29,30) benzoates. The rearrangement 94a ⟶ 95a and 94e ⟶ 95e is a selenol ester - seleninone transformation. The isomeric sulfur compounds 94 b - d and 94 f - h rearrange, too. This reaction was called thiol ester thiopyrone transformation.



94 a-d

95 a-d

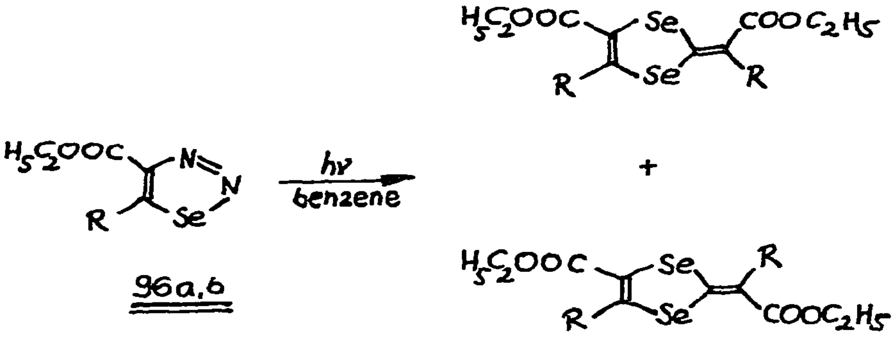


94 e-h

95 e-h

	X	Y	Z	R
94a	Se	CH	C	CH_3
b	S	CH	C	CH_3
c	S	N	C	H
d	S	CH	N	-
e	Se	CH	C	CH_3
f	S	CH	C	CH_3
g	S	N	C	H
h	S	CH	N	-

Meier and Menzer (74) photolysed 4-(ethoxycarbonyl)-1,2,3-selenadiazole (96) to obtain via a selenoketene intermediate 18 % of a 1 : 1 mixture of E- and Z-isomers of compound 97a.

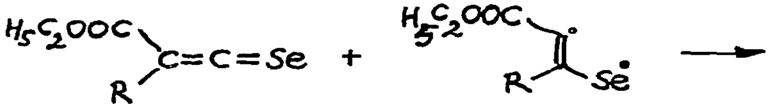


96a,b

97a,b

	a	b
R	H	CH_3

Similar photolysis of 96b proceded by Wolff rearrangement to give the selenoketene 98b, which dimerized with the unrearranged 1,3-diradical 99b to give E- and Z- 95b.



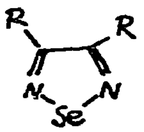
97a,b

98a,b

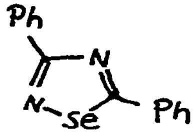
99a,b

	a	b
R	H	CH_3

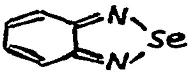
UV photolysis of 1,2,5-selenodiazoles 100 a - c, diphenyl-1,2,4-selenadiazole 101 and 2,1,3-benzoselenadiazole (102) at room temperature produced nitriles and selenium (75,76).



100 a-c



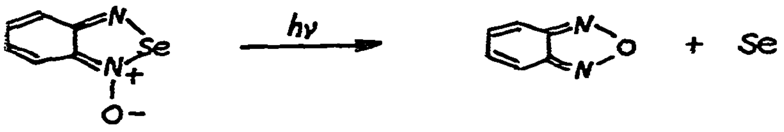
101



102

	a	b	c
R	H	CH_3	Ph

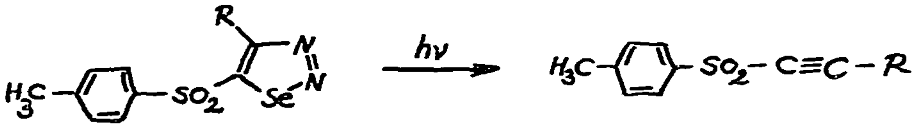
Irradiation ($\lambda > 390$ nm) of benzo [c] -1,2,5-selenadiazole 2-oxide (103) in methylene chloride at room temperature produced only benzofurazan (104, 96 % yield) and selenium (77,78). The mechanism of this reaction was studied in detail (79).



103

104

When the arylsulfonyl-1,2,3-selenadiazoles 105 were photolysed (80) in benzene solution elemental selenium and nitrogen were liberated to lead to the interesting alkynes 106:



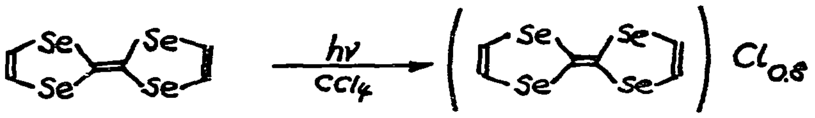
105

106

(42 - 64% yield)

$R = CH_3$, Ph

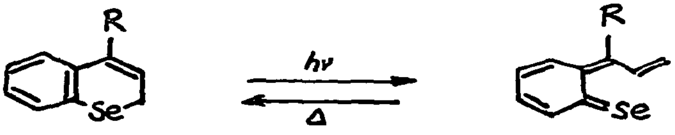
The photooxydation of tetraselenofulvalene (107) in CCl_4 solutions, providing a novel method for synthesizing high conductivity II-donor / halide salts 108, was described by Scott et al. (81).



107

108

Selenochromenes 109 a, b are the first and only photochromic organoselenium compounds mentioned in literature (81):



109 a,b

110 a,b

	a	b
R	H	Ph

Related photochromism is described in the literature for chromenes (87) and thiochromenes (84).

9. Miscellaneous

Aq. solutions of naphtaleneselenious and -selenic acids have been reported to be very sensitive to light (85).

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