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STABLE SELENOKETENES VIA SELENA-COPE REARRANGEMENT [1)]

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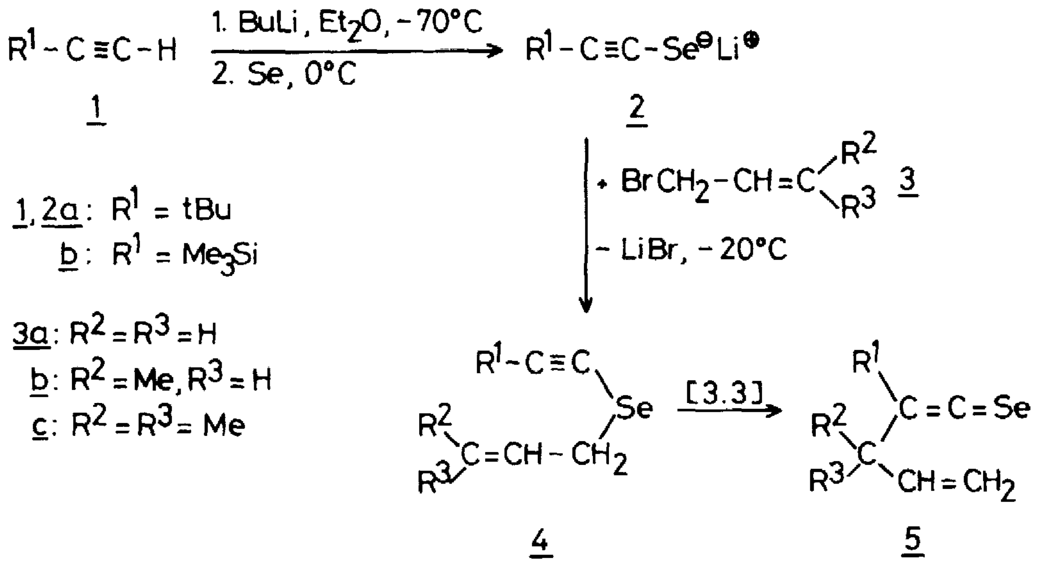
Summary - Selena-Cope rearrangement of selenides 4c,d leads to allyl(silyl)selenoketenes 5c,d, which could be fully characterised spectroscopically as well as by typical addition and cycloaddition reactions.

Selenoketenes have been invoked as transient species resulting from elimination of nitrogen from 1,2,3-selenadiazoles [2)] or from protonation of alkineselenolates [3)]. Their actual detection as highly labile compounds has been possible by flash-thermolysis [4)] or matrix-photolysis techniques [5)]. The only stable selenoketene reported so far is the bis(trimethylsilyl) derivative [6)], but from the chemistry of the analogous thioketene [7)] two silyl residues are known to change considerably the electronic character of the heterocumulene system.

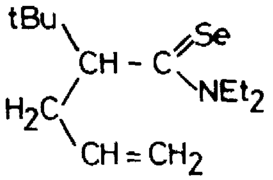
As rearrangement of alkinyl allyl sulfides by way of a [3.3]-sigmatropic shift has proven to provide a convenient access to thioketenes [8,9)], this approach seemed promising also for selenoketene synthesis [1)]. In an independent study, Sukhai and Brandsma [6)] indicated the formation of allyl(tert-butyl)selenoketene (5a) from allyl 3,3-dimethylbutinyl selenide (4a). We were unable to reproduce the reported heterocumulene IR-absorption at 1740 or 1750/cm [6)], but observed a band at 1710 cm^{-1} which may be reasonable for a selenoketene in the light of the reported values [4a,5a)]. Flash-distillation gave a blue oil with λ_{max} near 590 nm (isooctane), but the colour rapidly faded at room temperature. Our attempts to intercept the alleged selenoketene 5a with diethylamine led to a very low yield of selenoamide 6 (Table). Evidence for rearrangement of selenide 4b to 5b is less convincing since the IR-band at 1710 cm^{-1} is very weak and, after workup, selenide 4b seems to be rather stable (Table). In any case, the propensity of selenides 4a,b to yield selenoketenes via a [3.3]-sigmatropic process is less pronounced than with the analogous sulfides.

More promising candidates for selenoketene synthesis are the silyl ethinyl selenides 4c,d as in the corresponding sulfides the silyl substituent highly accelerates the rearrangement to thioketenes [8)]. Furthermore, the bulky allyl residues should give additional stabilization to the expected selenoketenes 5c,d. Selenides 4c,d are readily accessible from the alkine 1b following the usual pathway of selenium degradation and alkylation of the intermediate alkineselenolate 2. The crude products obtained after the usual workup [9)] are



1,2a: R^1 = tBu
b: R^1 = Me_3Si

3a: $R^2 = R^3 = H$
b: R^2 = Me, R^3 = H
c: $R^2 = R^3$ = Me



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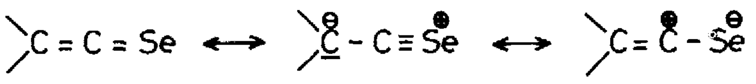
4,5	a	b	c	d
R^1	tBu	tBu	$SiMe_3$	$SiMe_3$
R^2	H	Me	Me	Me
R^3	H	H	H	Me

characterised by IR-absorptions at 2090 cm^{-1} for the C≡C bond. Heating at 60°C for 30 min (4c) or 5 hrs (4d) gives an essentially quantitative conversion into the purple selenoketenes 5c,d. These products can be stored in the refrigerator for weeks without appreciable decomposition. The structural assignment is based on the spectroscopic data (Table), where a UV band at rather long wavelength for the $n \to \pi^*$ transition and a ^{13}C-NMR signal at very low field prove the presence of the selenocarbonyl group. Both values are intermediate between the corresponding data for silylthioketenes [8,10)] and for alkyl(allyl)thioketenes [9)]. Hence it appears that the interaction within the cumulated π-electron system of selenoketenes is qualitatively analogous to their thio congeners [11)]:



5A 5B 5C

The importance of canonical formula 5B is substantiated by the occurence of $\delta_{C=C=Se}$ at rather high field (Table) and for 5d by a ^{77}Se resonance at δ = 49 downfield from external selenophene at δ = 0 pointing toward a slightly positive selenium [12)].

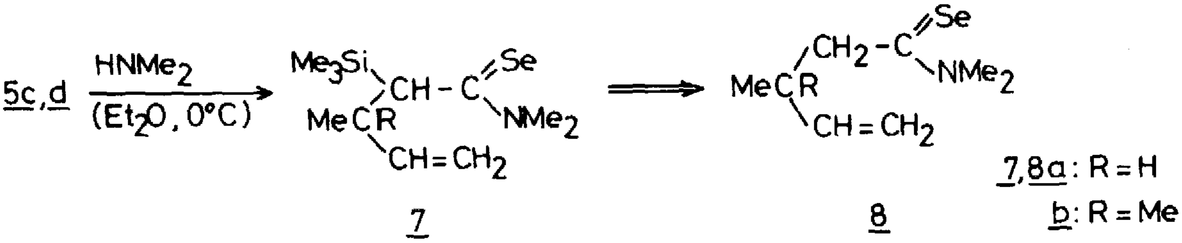
Additional evidence for the proposed selenoketene structures 5c,d could be obtained by the addition reactions with dimethylamine. Both heteroallenes were rapidly decolorized on addition of the amine at 0°C. Chromatographic workup (ethyl acetate/petroleum ether 1:20) led to moderate yields of the selenoamides 7a and 8a (Table) from 5c. Starting from 5d, only the desilylated selenoamide 8b was isolated with 7b or the zwitterionic primary addition product as probable precursors.

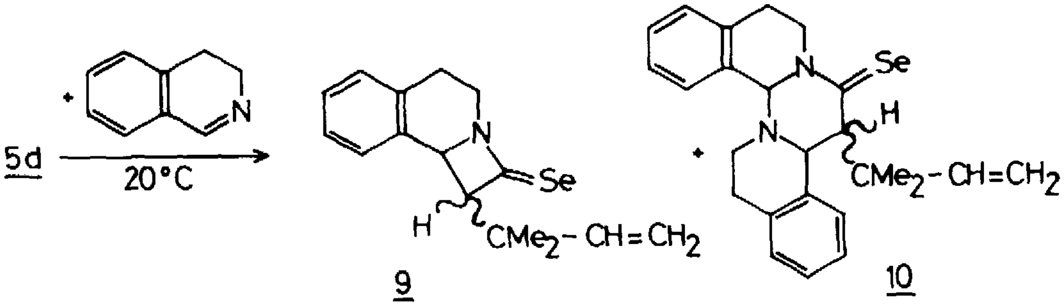
Table. Yields and characteristic data for the new compounds 13)

compd	yield [%]	b.p.[°C/torr] (m.p.[°C])	spectroscopic data (solvents: for IR-spectra KBr or neat, for ^{1}H- and ^{13}C-NMR measurements $CDCl_3$, for UV-spectra isooctane, unless otherwise noted)
4b	57	58-59/0.4	IR: ν 1660(C=C). - ^{1}H-NMR: δ 1.23(9H,tBu), 1.72(3H,$\underline{C}H_3$-CH), 3.30, 5.53(2+2H,CH-CH=CH_2). - ^{13}C-NMR: δ 129.2, 126.4(CH=CH_2), 109.4, 57.7(C≡C), 31.1, 30.9, 29.0, 17.7.
5c	25	49-56/0.3	IR: ν 1710(C=C=Se), 1250, ca. 850($SiMe_3$). - UV: λ 222(4.4), 291 (3.3), 554(1.3). - ^{13}C-NMR: δ 246.3(C=Se), 142.4, 113.3(CH=CH_2), 83.4($\underline{C}$=C=Se), 33.1, 22.2($CHCH_3$), -1.1($SiMe_3$).
5d	46	61-80/0.4	IR: ν 1690(C=C=Se), 1250, 850($SiMe_3$). - UV: λ 229(4.3), 291(3.4), 554(1.4). - ^{13}C-NMR: δ 247.9(C=Se), 147.1, 111.2(CH=CH_2), 89.2 ($\underline{C}$=C=Se), 36.3($\underline{C}Me_2$), 29.4($C\underline{C}H_3$), 0.8($SiMe_3$).
6	4	(47-48.5)	^{1}H-NMR (270 MHz): δ 1.07(9H, tBu), 1.25, 1.34(t,t,3+3 H,Et-CH_3), 2.32, 3.13(2 m's, 1+1H, allyl-CH_2), 2.86(d+d, J=12 and 2.7 Hz, 1H, α-CH), 3.38, 3.56, 3.98, 4.84(AB parts of 2 ABX_3 spectra, 1H each, Et-CH_2), 4.92-5.16, 5.56-5.76(m's, 3H, CH=CH_2). - MS (70 eV): m/e=275(20%, M^+ for ^{80}Se), 218(100, M - C_4H_9).
7a	5	(50-51)	IR: ν 1635, 1510, 1260, 1245, 840. - ^{1}H-NMR: 0.15(9H, $SiMe_3$), 3.28, 3.64(3+3H, NMe_2). a)
8a	12	oil	IR: ν 1640, 1520. - ^{1}H-NMR: δ 3.15, 3.55(NMe_2).
8b	37	oil	IR: ν 1635, 1515. - ^{1}H-NMR: δ 1.23(6H, CMe_2), 3.23, 3.58(3+3H, NMe_2).
9	32	(88-92)	IR: ν 1485. - UV (MeCN): λ 299(4.2), 383(2.3). - ^{1}H-NMR: δ 4.71 (1H, 9b-H). - ^{13}C-NMR: δ 207.1(C=Se), 144.1-113.5(Ar-C,CH=CH_2), 70.7, 61.9, 42.3, 37.8, 27.7, 25.2, 23.4.
10	19	(172-174)	IR: ν 1630, 1480. - UV (MeCN): λ 305(4.1), 408(2.3). - MS (70eV): m/e = 436 (1.5%, M^+ for ^{80}Se).

a) A second diastereomer with respect to the configuration at C-2,C-3 is present.

Desilylation is also observed in the cycloaddition with 3,4-dihydroisoquinoline. Chromatography (ethyl acetate/petroleum ether 1:9) yields a 1:1 and a 1:2 adduct. In both products, the selenoketene is obviously incorporated via the C=C bond since from the UV data and in the case of 9 also from the ^{13}C-NMR spectrum the presence of selenocarbonyl groups can be inferred (Table). Consequently, the 1:1 and 1:2 cycloadducts have to be formulated as a β-selenolactam 9 and a hexahydro-4-pyrimidineselenone 10, respectively. Thus, the azomethine furnishs the same types of cycloadducts with seleno as with allyl(silyl)thioketenes 10), however, the selenium functionality offers intriguing possibilities for further studies.





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References and Notes

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13) Except for 5c,d, which were not analyzed, satisfactory microanalytical results were obtained for the new compounds.

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