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SYNTHESIS OF 3,6-DIHALO-4,4-DIMETHYL-1,4-SELENASILAFULVENES

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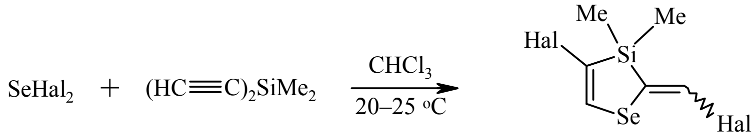
Selenium tetrahalides and Se_2Cl_2 add to acetylenes [1-3]. The electrophilic addition of organic selenyl halides to acetylenes is the major method for the synthesis of 2-halovinyl selenides [4-6]. There has been no information reported on the addition of selenium dihalides to acetylenes.

We have found that selenium dichloride and selenium dibromide generated *in situ* from elemental selenium and halogenating agents such as sulfuryl chloride and bromine may be used for the synthesis of new classes of heterocyclic compounds. The addition of selenium dichloride and selenium dibromide to dimethyldiethynylsilane leads to previously unreported heterocyclic systems, namely, 3,6-dihalo-4,4-dimethyl-1,4-selenasilafulvenes **1** and **2** in 70-72% yield.



1, **2**

1 Hal = Cl, **2** Hal = Br

This reaction proceeds at room temperature in chloroform over 3-4 h. The structures of **1** and **2**, which are mixtures of *Z*- and *E*-isomers, were demonstrated using ^1H, ^{13}C, ^{29}Si, and ^{77}Se NMR spectroscopy and supported by elemental analysis. The ratio of the *Z*- and *E*-isomers was established using NMR spectroscopy. The NMR spectra were taken in $CDCl_3$ at 400 (^1H), 100 (^{13}C), 79 (^{29}Si), and 76 MHz (^{77}Se).

4,4-Dimethyl-3,6-dichloro-1,4-selenasilafulvene (1) was obtained in 72% yield as a 5:1 mixture of *Z*- and *E*-isomers. For the *Z*-isomer: ^1H NMR spectrum, δ, ppm, (*J*, Hz): 7.15 (1H, d, $J = 1$, =CHSe); 6.64 (1H, d, $J = 1$, =CHCl); 0.37 (6H, s, CH_3). ^{13}C NMR spectrum, δ, ppm: 134.60 (SiCSe), 130.04 (=CHSe), 125.52 (SiCCl), 122.69 (=CHCl), -2.35 (CH_3Si). ^{29}Si NMR spectrum, δ, ppm: 5.6. ^{77}Se NMR spectrum, δ, ppm, (*J*, Hz): 492 ($^2J_{Se–H} = 54$, $^3J_{Se–H} = 12$). For the *E*-isomer: ^1H NMR spectrum, δ, ppm: 7.10 (1H, s, =CHSe); 6.61 (1H, s, =CHCl); 0.49 (6H, s, CH_3). ^{13}C NMR spectrum, δ, ppm: 132.88 (SiCSe), 129.42 (=CHSe), 124.88 (SiCCl), 122.69 (=CHCl), -3.95 (CH_3Si). ^{29}Si NMR spectrum, δ, ppm: 7.1. ^{77}Se NMR spectrum, δ, ppm, (*J*, Hz): 504 ($^2J_{Se–H} = 55$, $^3J_{Se–H} = 9$). Found, %: C 28.10; H 3.30; Cl 28.12; Se 31.04; Si 11.04. $C_6H_8Cl_2SeSi$. Calculated, %: C 27.92; H 3.10; Cl 27.53; Se 30.59; Si 10.86.

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3,6-Dibromo-4,4-dimethyl-1,4-selenasilafulvene (2) was obtained in 70% yield as a 6:1 mixture of *Z*- and *E*-isomers. For the *Z*-isomer: ^{1}H NMR spectrum, δ, ppm, (*J*, Hz): 7.43 (1H, d, *J* = 1, =CHSe); 6.93 (1H, d, *J* = 1, =CHBr); 0.35 (6H, s, CH_3). ^{13}C NMR spectrum, δ, ppm: 139.76 (SiCSe), 132.29 (=CHSe), 112.45 (SiCBr), 111.44 (=CHBr), -2.49 (CH_3Si). ^{29}Si NMR spectrum, δ, ppm: 7.7. ^{77}Se NMR spectrum, δ, ppm, (*J*, Hz): 553 ($^2J_{Se–H}$ = 54, $^3J_{Se–H}$ = 14). For the *E*-isomer: ^{1}H NMR spectrum, δ, ppm: 7.35 (1H, s, =CHSe); 6.80 (1H, s, =CHBr); 0.49 (6H, s, CH_3). ^{13}C NMR spectrum, δ, ppm: 133.18 (SiCSe), 131.40 (=CHSe), 111.38 (SiCBr), 109.64 (=CHBr), -3.88 (CH_3Si). ^{29}Si NMR spectrum, δ, ppm: 6.8. ^{77}Se NMR spectrum, δ, ppm, (*J*, Hz): 568 ($^2J_{Se–H}$ = 56, $^3J_{Se-H}$ = 11). Found, %: C 21.93; H 2.48; Br 46.15; Se 21.80; Si 8.09. $C_6H_8Br_2SeSi$. Calculated, %: C 20.76; H 2.31; Br 46.12; Se 22.74; Si 8.07.

REFERENCES

1. R. F. Riley, J. Flato, and D. Bengels, *J. Org. Chem.*, **27**, 2651 (1962).
2. W. Reid and G. Sell, *Synthesis*, 447 (1976).
3. V. G. Lendel, B. I. Pak, V. Yu. Migalina, P. Kuchi, M. Dzurilla, and P. Christian, *Zh. Org. Chem.*, **26**, 1849 (1990).
4. G. H. Schmid, in: S. Patai (editor), *The Chemistry of the Carbon-Carbon Triple Bond*, John Wiley & Sons, Chichester (1978), p. 275.
5. T. G. Back, in: D. Liotta (editor), *Organoselenium Chemistry*, John Wiley & Sons, New York (1987), p. 1.
6. V. A. Potapov, S. V. Amosova, B. V. Petrov, A. A. Starkova, and R. N. Malyushenko, *Sulfur Lett.*, **21**, 109 (1998).