# Synthesis of Dialkenyl Dichalcogenides *via* Alkenechalcogenolate Ions Generated by Treating Ketone *p*-Toluenesulfonylhydrazones with a Base and Elemental Chalcogen

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Alkeneselenolate and alkenetellurolate ions were generated by treating ketone *p*-toluenesulfonylhydrazones possessing an α-methylene or an α-methine group with *t*-BuOK and elemental selenium or tellurium, respectively, at 110-150 °C, and were converted into dialkenyl dichalcogenides by aerobic oxidation.

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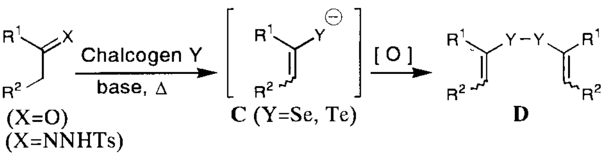
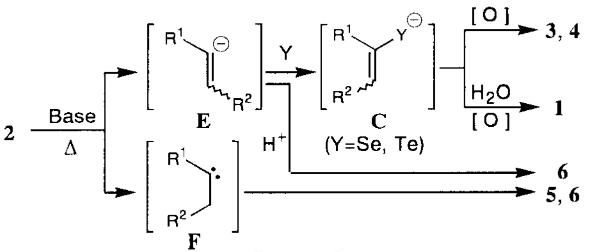
Recently, dialkenyl disulfides have been well recognized as the precursors of various naturally-occurring heterocycles and the synthetic precursors of thiocarbonyl compounds.[1] However, the lack of convenient methods for preparation of dialkenyl diselenides and ditellurides **D** has impeded the synthetic use of such compounds as the precursors of various heterocycles.[2] During our synthetic studies on chalcogenocarbonyl compounds, we have expected that the reaction of alkenyl carbanions generated by Bamford-Stevens reaction of ketone *p*-toluenesulfonylhydrazones **B** possessing an α-methylene or an α-methine group[3] with elemental chalcogen would afford alkenechalcogenolate ions **C**. In this paper, we would like to describe a novel and convenient synthesis of dialkenyl dichalcogenides **D** by the procedure involving the generation of alkenechalcogenolate ions **C**(Y=Se, Te) by treating **B** with *t*-BuOK and elemental selenium or tellurium and the subsequent aerobic oxidation of **C**.



Scheme 1.

Ketone *p*-toluenesulfonylhydrazones **2**, prepared from ketones **1**, were treated with *t*-BuOK and elemental selenium or tellurium in DMF or HMPA at 110-150 °C under an Ar atmosphere, and the reaction mixture was exposed to air at room temperature. After the usual workup and chromatographic separation, dialkenyl diselenides **3**(Y=Se) or ditelllurides **4**(Y=Te), respectively, were obtained in modest yields along with substrates **2**, olefins **5**,[3b] olefins **6**, and ketones **1**.[4] In most cases, addition of $Et_2NH$ to the reaction media was much effective for preparation of **3**. Table 1 gives all the results of the reactions. Especially, treatment of acetophenone *p*-toluenesulfonylhydrazone (**2a**) with *t*-BuOK and elemental selenium gave selenophene **7**,[5] which was assumed to be afforded through [3,3] sigmatropic rearrangement of **3a**. Unexpectedly, treatment of **2e** with *t*-BuOK and elemental selenium that was preactivated by sonication gave novel 1,2,5-triselenepin **9** in 35% yield along with several inseparable products containing **3e**. The structure of **9** was finally determined by X-ray crystallographic analysis.[6]

Treatment of a HMPA solution of **2b** with *t*-BuOK, $Et_2NH$, and elemental selenium and then with allyl bromide gave the corresponding alkenyl allyl selenide (**11b**, 62%), and the similar treatment of **2b** with *t*-BuOK, elemental tellurium, and then with iodomethane also gave alkenyl methyl telluride (**12b**, 33%). The physical data of **11b** and **12b** were identical with those of the authentic samples obtained by the stepwise treatment of dialkenyl diselenides **3b**(Y=Se) or ditellurides **4b**(Y=Te) with a hydride and the same alkylating agent. Furthermore, quenching the reaction of **2b** with *t*-BuOK-elemental selenium using aqueous HCl solution in place of aerobic exposure afforded deoxybenzoin (**1b**) in 40% yield. These results supported that alkenechalcogenolate ions **C** were predominantly generated by the reaction of **2** with *t*-BuOK and elemental chalcogen.[3,7] Byproducts of the reactions were also given through protonation of alkenyl anions **E**, dimerization of carbenes **F** generated from **2**, and protonation of chalcogenolate ions **C** as shown in Scheme 2.



Scheme 2.

When the selenation reaction was applied to the substrates lacking an α-methylene group (**2f**, **2g**), dimeric olefins were obtained as main products, and only a trace amount of selone **10**[8] was afforded in the case starting from **2g**. The treatment of **2b** with *t*-BuOK and elemental selenium in the presence of an excess amount of 2,3-dimethyl-1,3-butadiene also gave a mixture of **3b**, **5b**, **6b**, and **1b**, and the [4+2] cycloadducts of deoxybenzoinselone with the diene were not found at all. These result indicated that the reaction of carbenes **F** with elemental chalcogen was only a minor pathway for the chalcogenation.

In conclusion, we have found a novel and convenient method for synthesis of dialkenyl dichalcogenides **D** by starting from ketone *p*-toluenesulfonylhydrazones and elemental chalcogen. Further attempts for thermal conversion of dialkenyl dichalcogenides **D** into the corresponding chalcogenophenes are in progress in our laboratory.

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## References and Notes

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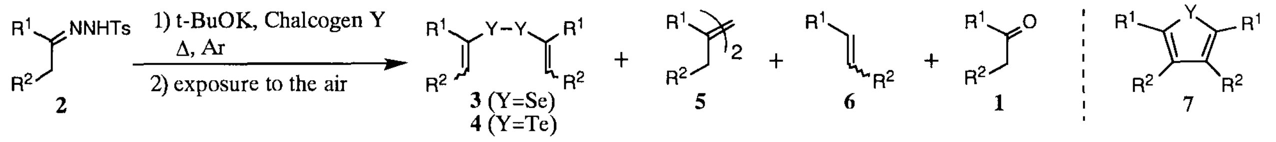
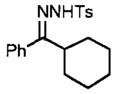
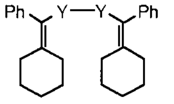
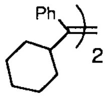
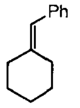
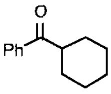
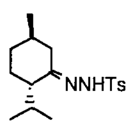
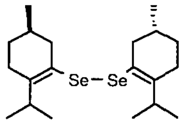
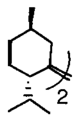
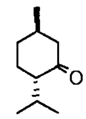
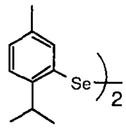
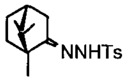
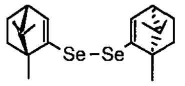
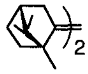
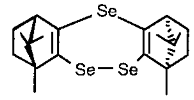
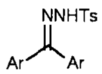
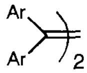
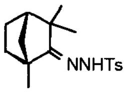
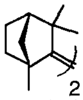
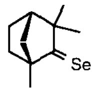
**Table 1.** Treatment of Ketone *p*-Toluenesulfonylhydrazones **2** with *t*-BuOK and Elemental Chalcogen [a]



| Substrate | | | Y | Solvent | $Et_2NH$ | Temp | Time | Product (Yield /%) [b] | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $R^1$ | $R^2$ | 2 | | | (mol amt.) | / °C | / h | **3, 4** | **5** | **6** | **1** | others |
| $C_6H_5$ | H | **2a** | Se | DMF | 0 | 130 | 3 | trace (**3a**) | 20 (**5a**) [c] | 0 | 0 | 8 (7: Y=Se) |
| $C_6H_5$ | $C_6H_5$ | **2b** | Se | DMF | 0 | 140 | 3 | 43 (**3b**) [c] | 17 (**5b**) [c] | trace (**6b**) [c] | 10 (**1b**) | |
| | | | Se | HMPA | 0 | 150 | 0.5 | 56 (**3b**) [c] | trace (**5b**) [c] | 20 (**6b**) [c] | 10 (**1b**) | |
| | | | Se | HMPA | 2.5 | 120 | 0.5 | 70 (**3b**) [c] | trace (**5b**) [c] | 23 (**6b**) [c] | 2 (**1b**) | |
| | | | Te | DMF | 0 | reflux | 3 | 45 (**4b**) [d] | 0 | 25 (**6b**) [c] | 0 | |
|  | | | | | | | |  |  |  |  | |
| **2c** | | | Se | HMPA | 2.5 | 120 | 2.5 | 52 (**3c**: Y=Se) | 14 (**5c**) [c] | 30 (**6c**) | 0 | |
| | | | Te | DMF | 0 | reflux | 3 | 26 (**4c**: Y=Te) | 0 | 24 (**6c**) | 5 (**1c**) | |
|  | | | | | | | |  |  | |  |  |
| **2d** | | | Se | HMPA | 2.5 | 100 | 3 | 70 (**3d**) | 19 (**5d**) | | trace (**1d**) | 10 (**8**) |
|  | | | | | | | |  |  | | |  |
| **2e** | | | Se | HMPA | 2.5 | 120 | 3 | 64 (**3e**) | 30 (**5e**) | | | 5 (**9**) |
| | | | Se [e] | DMF | 0 | 110 | 3 | trace (**3e**) | trace (**5e**) | | | 35 (**9**) |
|  | | | | | | | | |  | | | |
| **2f** (Ar=*p*-$CH_3OC_6H_4$) | | | Se | HMPA | 0 | 120 | 3 | | 90 (**5f**) | | | |
|  | | | | | | | | |  | | |  |
| **2g** | | | Se | DMF | 0 | 140 | 14 | | 64 (**5g**) | | | 0.5 (**10**) |

[a] A solution of **2** was treated with *t*-BuOK (2.5 mol amt.) and elemental chalcogen (2.5 mol amt.) at 110-150 °C under an Ar atmosphere, and the reaction mixture was cooled and exposed to air for 5-6 h. [b] Isolated yields. [c] Combined yield of *E*- and *Z*-isomers. [d] A mixture of *E*- and *Z*-isomers (about 1:1) . [e] Preactivated by sonication.

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4 The physical data of **3**, **4**, **8**, **9**, **11b**, and **12b** are available as supplementary materials.

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6 X-ray crystallographic data for **9**: $C_{20}H_{28}Se_3$, Mw=505.32, Colorless prism, monoclinic, $P2_1$(#4), a=7.857(3), b=14.637(5), c=9.005(4) Å, β=97.09(3)°, V=1027.7(6) Å$^3$, Z=2, $D_{calc}$=1.633 g/cm$^3$, μ(MoKα)=53.68 cm$^{-1}$, R=0.025, Rw=0.026.

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