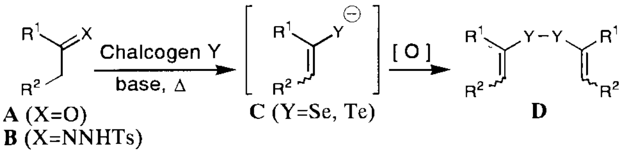
Synthesis of Dialkenyl Dichalcogenides *via* Alkenechalcogenolate Ions Generated by Treating Ketone *p*-Toluenesulfonylhydrazones with a Base and Elemental Chalcogen

Kazuaki Shimada, Mitsuharu Asahida, Ken Takahashi, Yoshitaka Sato, Shigenobu Aoyagi, Yuji Takikawa,* and Chizuko Kabuto†
Department of Applied Chemistry and Molecular Science, Faculty of Engineering, Iwate University, Morioka, Iwate 020-8551
†Instrumental Analytical Center for Chemistry, Faculty of Science, Tohoku University, Sendai, Miyagi 980-8578

(Received February 13, 1998; CL-980105)

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.

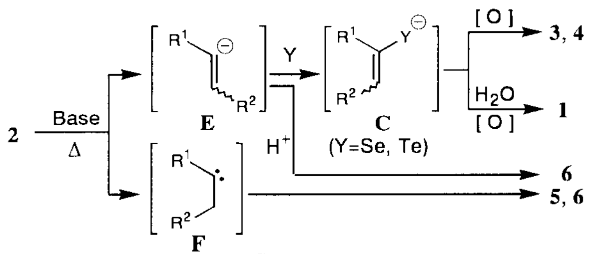
Recently, dialkenyl disulfides have been well recognized as the precursors of various naturally-occurring heterocycles and the synthetic precursors of thiocarbonyl compounds.[1] However, the lack of convenient methods for preparation of dialkenyl diselenides and ditellurides **D** has impeded the synthetic 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.

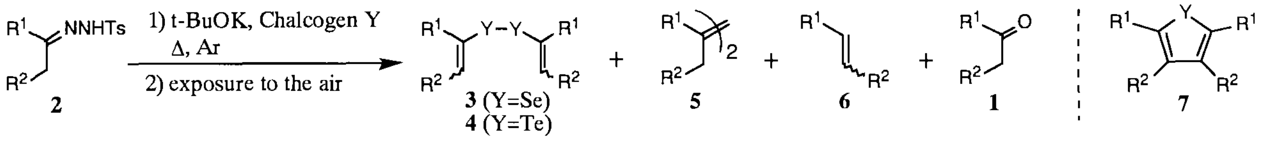
In conclusion, we have found a novel and convenient method for synthesis of dialkenyl dichalcogenides **D** by starting from ketone *p*-toluenesulfonylhydrazones and elemental chalcogen. Further attempts for thermal conversion of dialkenyl dichalcogenides **D** into the corresponding chalcogenophenes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

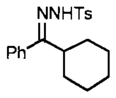
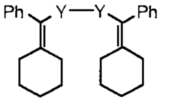
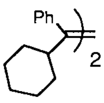
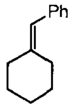
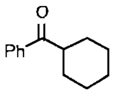
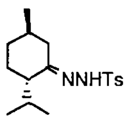
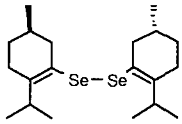
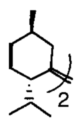
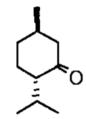
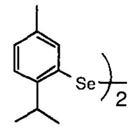
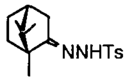
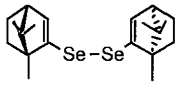
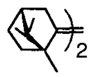
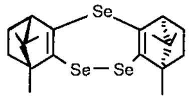
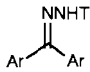
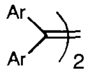
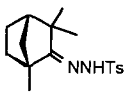
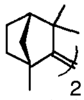
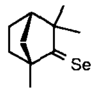
This work was partially supported by Grant-in-Aid for Scientific Research (No. 07651044) from the Ministry of Education, Science, Sports, and Culture.

References and Notes

1 a) H. Boelens and L. Brandsma, *Requeil*, **91**, 141 (1972). b) F. C. V. Larsson, L. Brandsma, and S. -O. Lawesson, *Requeil*, **93**, 258 (1974). c) Y. Tamaru, T. Harada, and Z. Yoshida, *J. Am. Chem. Soc.*, **100**, 1923 (1978). d) P. Metzner, *Synthesis*, **1992**, 1185. e) W. Schroth, E. Hintzsche, R. Spitzner, H. Irngartinger, and V. Siemund, *Tetrahedron Lett.*, **35**, 1973 (1994).

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.

2 a) J. N. Marx and L. R. Norman, *Tetrahedron Lett*., **1973**, 2867. b) S. Kato, T. Komuro, T. Kanda, H. Ishihara, and T. Murai, *J. Am. Chem. Soc*., **115**, 3000 (1993). c) J. V. Comasseto, W. L. Lo, N. Petragnani, and H. A. Stefani, *Synthesis*, **1997**, 373, and the references cited therein.

3 a) W. R. Bamford and T. S. Stevens, *J. Chem. Soc*., **1952**, 4735. b) R. H. Shapiro, "Organic Reactions", ed by W. G. Dauben, (1976), Vol. 23, p. 405, and the references cited therein.

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

5 I. Lalezari, A. Shafiee, F. Rabet, and M. Yalpani, *J. Heterocycl. Chem*., **10**, 953 (1973).

6 X-ray crystallographic data for **9**: $C_{20}H_{28}Se_3$, M_w=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, R_w=0.026.

7 A. R. Chamberlin and S. H. Bloom, "Organic Reactions", ed by L. A. Paquette, (1990), Vol. 39, p. 1.

8 a) T. G. Back, D. H. R. Barton, M. R. Britten-Kelly, and F. S. Guziec, Jr., *J. Chem. Soc., Chem. Commun*., **1975**, 539. b) T. G. Back, D. H. R. Barton, M. R. Britten-Kelly, and F. S. Guziec, Jr., *J. Chem. Soc., Perkin Trans. 1*, **1976**, 2079. c) F. S. Guziec, Jr. and C. A. Moustakis, *J. Org. Chem*., **49**, 189 (1984). d) R. Okazaki, A. Ishii, and N. Inamoto, *J. Chem. Soc., Chem. Commun*., **1983**, 1429. e) A. Ishii, R. Okazaki, and N. Inamoto, *Bull. Chem. Soc. Jpn*., **61**, 861 (1988).