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Tetraethylammonium tetraselenotungstate: a new and efficient selenium transfer reagent for the chemoselective synthesis of functionalised diselenides

Vadivelu Saravanan, Emmanuel Porhiel and Srinivasan Chandrasekaran*

Department of Organic Chemistry, Indian Institute of Science, Bangalore 560 012, India

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Dedicated to Professor S. Swaminathan on the occasion of his 80th birthday

Abstract—A variety of functionalised organodiselenides were prepared in excellent yields from the corresponding halides and activated alcohols on treatment with tetraethylammonium tetraselenotungstate **1** under very mild conditions. © 2003 Elsevier Science Ltd. All rights reserved.

The growing field of organoselenium chemistry with its many applications, has initiated a synthetic need for efficient reagents for the synthesis of organoselenium compounds. Notably, organic diselenides have attracted much attention as intermediates in organic synthesis.[1] Various methods are available for the synthesis of these compounds.[2–7] Among them, the most important routes involve the reaction of metal diselenides[2,3] with alkyl halides, dimerisation of selenocyanates,[4–6] and preparation of selenols which can be subjected to further oxidation.[7] Methods involving the use of metal diselenides have generally been carried out in the presence of strong reducing agents[2] and basic conditions.[3] This calls for a new chemoselective method, which can facilitate the synthesis of diselenides rapidly under very mild conditions. Herein we report our successful results on the use of tetraethylammonium tetraselenotungstate, $[Et_4N]_2WSe_4$ **1** as a new selenium transfer reagent and its application to the synthesis of functionalised diselenides.

Müller and co-workers[8] first reported the reagent **1** and we prepared **1** by a slight modification of the procedure reported by Kollis and O'Neal.[9] The reaction of alkyl halides with **1** (1.1 equiv., CH_3CN, 28°C, 5–90 min) furnished after purification the corresponding diselenides in high yields (81–95%). The results are summarised in Table 1. As can be seen from Table 1, except in the case of hydroxy bromide **8** (entry 8), all the substrates reacted with great facility in a short period of time (5–45 min). Special mention may be made of successful reaction of the substrates **2b**, **2c** and **2e**, which contain easily reducible functional groups such as cyano, ester and keto functionalities. Methods involving the use of metal diselenides and reducing agents[2,5a] can not be applied successfully in some of these cases. This type of chemoselectivity obtained at room temperature is unusual. However, in the case of reactive alkyl halides such as *p*-nitrobenzyl bromide **14** and ethyl bromoacetate **17** (entries 11, 12), a mixture of the corresponding monoselenides **15** and **18** and diselenides **16** and **19**, respectively, were formed where the nitro and ester groups remain untouched.[10] The facile formation of cyclic diselenide **7** in the form of an eight membered ring holds promise for further exploration of **1** in intramolecular cyclisation processes. The selenium transfer reaction of glucose and lactose derived anomeric bromides **10** and **12** with **1** can be used efficiently for the synthesis of the β-diselenides **11** and **13**, respectively, in high yields. This would provide entry to carbohydrate-derived diselenides and derivatives.

The relative rates of reaction of **1** with alkyl halides appear to follow the general pattern of the bimolecular substitution pathway.[11] The mechanism of alkylation of selenometallates of this type has not been studied and is poorly understood. A tentative mechanism based on the analogous reaction of tetrathiotungstate[12] with alkyl halides is presented in Scheme 1. The first step

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* Corresponding author. Tel.: +91-80-3942404; fax: +91-80-3600529; e-mail: scn@orgchem.iisc.ernet.in

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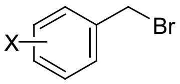
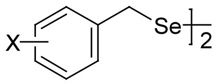
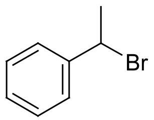
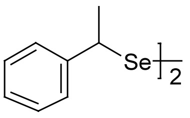
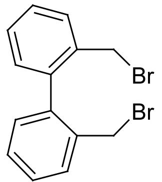
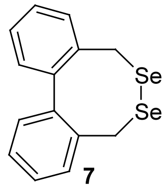
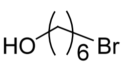
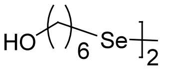
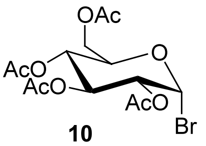
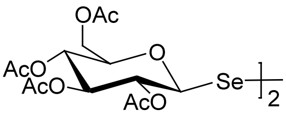
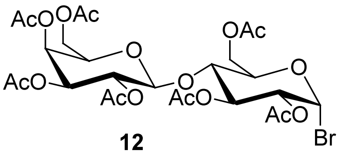
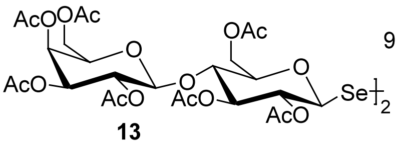
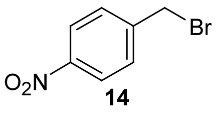
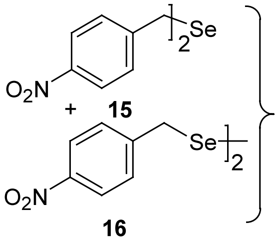
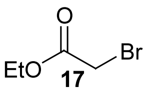
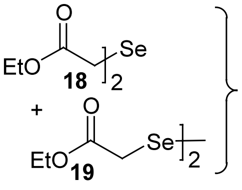
Table 1. Synthesis of diselenides from alkyl halides

Entry	Starting material	t/min	Product	Yield (%)[a,b]
				
1	**2a** X = H	5	**3a**	92
2	**2b** X = *p*-CN	5	**3b**	95
3	**2c** X = *p*-CO_2Et	5	**3c**	84
4	**2d** X = *o*-OMe	5	**3d**	91
5	**2e** X = *p*-COPh	15	**3e**	81
6	 **4**	5	 **5**	92
7	 **6**	30	 **7**	89
8	 **8**	90	 **9**	89
9	 **10**	45	 **11**	91
10	 **12**	45	 **13**	92
11	 **14**	5	 **15** + **16**	82 (1:1)
12	 **17**	30	 **18** + **19**	84 (1:1)

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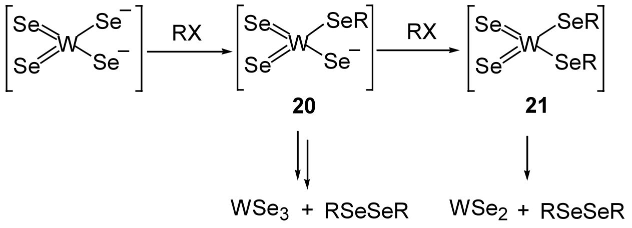
[a] Refers to isolated yield.

[b] All the products exhibited the expected analytical and spectral data

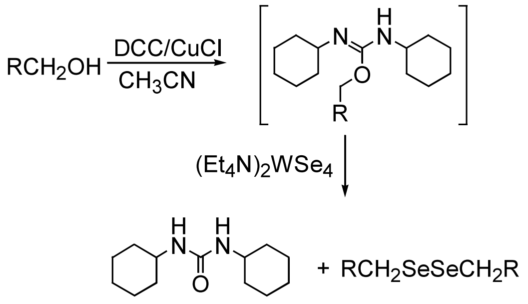


Scheme 1.

involves Se⁻ alkylation to form a mono alkylated species **20** or the dialkylated species **21** which can then undergo an internal redox reaction with oxidation of the selenium ligand and concomitant reduction of the metal centre.[13]

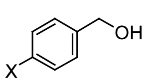
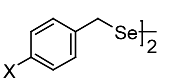
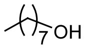
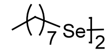
Since halides are frequently prepared from alcohols, conversion of alcohols to the corresponding diselenides would be an interesting methodology. Accordingly alcohols were activated with dicyclohexylcarbodiimide and a catalytic amount of CuCl to form the isourea in situ[14] which on further treatment with **1** in CH_3CN at room temperature afforded the corresponding diselenides in good yields (Scheme 2).

The results are summarised in Table 2. The reaction of benzylic alcohols (entries 1–3) was much faster than *n*-octanol (entry 4). The reaction of cyclohexanol did not furnish any product even after 96 h.



Scheme 2.

Table 2. Synthesis of diselenides from alcohols

Entry	Starting material	t/h	Product	Yield (%)[a,b]
				
1	**22a** X = H	8	**23a**	81
2	**22b** X = Cl	8	**23b**	75
3	**22c** X = OMe	8	**23c**	71
4	 **24**	36	 **25**	84

[a] Refers to isolated yield.

[b] All the products exhibited the expected analytical and spectral data.

In conclusion, we have demonstrated the synthetic utility of tetraselenotungstate **1** as a novel reagent for selenium transfer reactions as applied to the synthesis of functionalised diselenides. The present methodology compares favourably and compliments the existing methods. Further synthetic applications and mechanistic studies involving the use of **1** with organic substrates are currently under investigation.

Experimental

Procedure for the synthesis of tetraselenotungstate:[9] K_2Se_3 (6.3 g, 20 mmol) and $W(CO)_6$ (3.42 g, 10 mmol) were dissolved in DMF (250 ml) and the solution was heated to 90°C for 1 h. Et_4NBr (4.1 g, 20 mmol) was added, and the solution was filtered, THF (150 ml) was added, and, after storage at 4°C overnight, $(Et_4N)_2WSe_4$ was isolated as a red solid (4.6 g, 60%), mp: 120°C (decomp.); Raman [cm^{-1}]:[8] 309, 281, 107; UV–vis [NaOH]:[8] λ_{max}, nm, 463, 313, 241.

Typical experimental procedure for the reaction of 1 with alkyl halides: To a stirred solution of $(Et_4N)_2WSe_4$, **1** (1.1 mmol) in CH_3CN (6 ml) was added slowly a solution of the alkyl halide (1 mmol) in CH_3CN (1 ml) at room temperature. After completion of the reaction (TLC, 5–90 min) the solvent was removed in vacuo and the black residue was extracted with CH_2Cl_2–Et_2O (1:9, 5×20 ml) and filtered through a Celite pad. The filtrate was concentrated and the crude product was purified by column chromatography or recrystallised to reveal the product.

Procedure for synthesis of diselenides directly from alcohols: A mixture of alcohol (1 mmol), DCC (1.1 mmol) and CuCl (5 mol%) were stirred at room temperature. After completion of the reaction (TLC, 6–12 h), CH_3CN (5 ml) and $(Et_4N)_2WSe_4$ **1** (1.1 mmol) were added and the reaction mixture was stirred at room temperature until the starting material disappeared. The reaction mixture was worked-up as described above.

Acknowledgements

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