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Efficient Conversion of Vicinal Diols to Alkenes by Treatment of the Corresponding Dimesylates with a Catalytic, Minimally Fluorous, Recoverable Diaryl Diselenide and Sodium Borohydride

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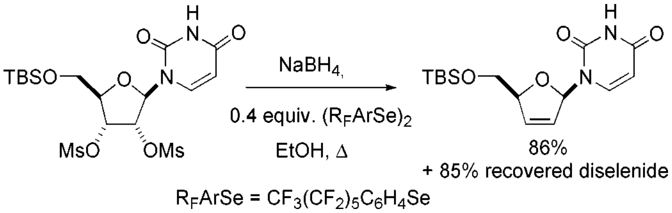
ABSTRACT



In conjunction with sodium borohydride as stoichiometric reagent a catalytic quantity of bis(4-perfluorohexylphenyl) diselenide converts vicinal dimesylates to the corresponding alkenes in good yield on warming in ethanol. The diselenide is recovered in high yield by continuous fluorous extraction.

Clive and his group have described a protocol for the elimination of vicinal dimesylates to alkenes by treatment with areneselenide anions or with telluride dianion.[1,2] The nucleophiles were generated in situ by reduction of the diselenide or of tellurium, respectively, with lithium triethylborohydride or with sodium in liquid ammonia. Although, in view of the reasonable mechanisms proposed, the diselenide and tellurium metal, respectively, are necessarily regenerated in the course of the reaction, only one example, using bis(2,4-dimethoxyphenyl) ditelluride with ethanolic sodium borohydride as stoichiometirc reductant, was reported as being successful under catalytic conditions.[1] On a larger scale the use of stoichiometric organoselenium and tellurium reagents mandates their recovery and recycling for both economic and environmental reasons. Furthermore, in the case of low polarity products, separation from large quantities of diphenyl diselenide by silica gel chromatography can also be problematic. Here we describe a catalytic variant on Clive's protocol, employing a minimally fluorous diselenide, recoverable by continuous fluorous extraction. We also make use of sodium borohydride in ethanol as the reducing system and solvent, which eliminates the need for highly anhydrous media and for the addition of HMPA, which are characteristic of Clive's superhydride/THF/HMPA system.[1,2]

Previously, we have described the preparation of the highly crystalline, minimally fluorous diselenide **1** and its application as a recoverable source of areneselenol in stannane-

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(1) Clive, D. L. J.; Wickens, P. L.; Sgarbi, P. W. M. *J. Org. Chem.* **1996**, *61*, 7426.

(2) Clive, D. L. J.; Sgarbi, P. W. M.; Wickens, P. L. *J. Org. Chem.* **1997**, *62*, 3751.

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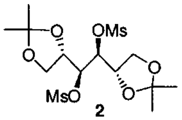
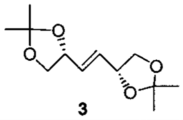
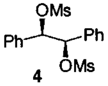
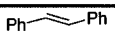
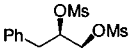
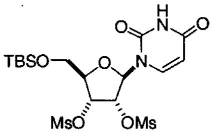
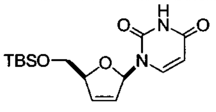
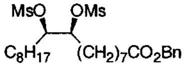
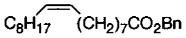
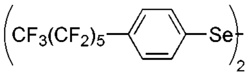
Table 1. Fluorous Selenide Mediated Eliminations[a]

substrate	product	stoichiometric reaction		catalytic reaction[b]	
		product yield	recovered **1**	product yield	recovered **1**
 **2**	 **3**	78%	92%	74%	76%
 **4**	 **5**	89%	89%	81%	72%
 **6**	 **7**	84%	85%	81%	70%
 **8**	 **9**	88%	89%	86%[c]	85%[c]
 **10**	 **11**	96%	91%	99%	88%

[a] With the exception of **6**, all dimesylates and alkenes were as described in the literature[1,2,11,12] or were identical to commercial samples. [b] Unless otherwise stated 0.2 molar equiv of **1** was used (see Typical Procedure). [c] 0.4 molar equiv of **1** was used (see text).

mediated radical chain reactions.[3,4] We have also reported a protocol for the dehydrogenation of ketones and esters using a selenenyl chloride derived from **1**.[5] For solubility reasons the fluorous chains in **1** were limited to six carbons, resulting in a fluorine content of 52%, which is below the nominal minimum of 60% usually considered necessary for ready extraction into fluorous solvents.[6−8] We therefore termed these diselenides "minimally" fluorous and developed a convenient protocol for their recovery involving brief continuous extraction of the organic solvent by the fluorous phase in a water-jacketed continuous extractor.[4] Curran has termed such minimally fluorous substances "light" fluorous reagents and has presented an alternative protocol for their recovery involving chromatography over fluorous silica gel.[9]



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A protocol for elimination was readily developed in which an orange ethanolic solution of **1** was reduced with excess $NaBH_4$ under an inert atmosphere to give a colorless solution of the selenide,[10] followed by addition of the dimesylate and refluxing until completion (5−6 h). After aqueous work up the organics were partitioned between dichloromethane and FC-72 in the jacketed continuous extractor, which permitted recovery of the pure diselenide and greatly facilitated the chromatgraphic purification of the alkene. As is evident from Table 1, the alkenes were obtained in good yield in all cases and the diselenide was recovered efficiently. We then turned to the development of a catalytic variant on this protocol by reducing gradually the amount of diselenide employed. Eventually, we settled on the use of 0.2 molar equiv of **1** in 0.02 M ethanolic solution with the use of a 10-fold excess (wrt **1**) of sodium borohydride.[13] The results presented in Table 1 indicate that these conditions were satisfactory in every instance but one; in the case of the nucleoside 2′,3′-dimesylate **8**, the yield was depleted by the formation of several byproducts, one of which was identified as **12**. On the grounds that these byproducts arise by competing intramolecular S_N2 attack by the base on the 2′-*O*-mesylate and then elimination (and desilylation), the amount of **1** was doubled to 0.4 equiv, which effectively restored the yield to

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(3) Crich, D.; Hao, X. *Org. Lett.* **1999**, *1*, 269.

(4) Crich, D.; Hao, X.; Lucas, M. *Tetrahedron* **1999**, *55*, 14261.

(5) Crich, D.; Barba, G. R. *Org. Lett.* **2000**, *2*, 989.

(6) Horvath, I. T. *Acc. Chem. Res.* **1998**, *31*, 641.

(7) de Wolf, E.; van Koten, G.; Deelman, B.-J. *Chem. Soc. Rev.* **1999**, *28*, 37.

(8) Curran, D. P. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1174.

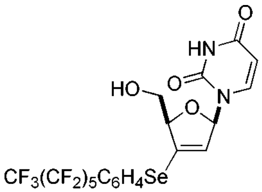
(9) Curran, D. P.; Luo, Z. *J. Am. Chem. Soc.* **1999**, *121*, 9069.

(10) Although we have not attempted any demonstration, we assume that the true nucleophile is the arylseleno(triethoxy)borate: Miyashita, M.; Hoshino, M.; Yoshikoshi, A. *Tetrahedron Lett.* **1988**, *29*, 347

(11) Habich, D.; Barth, W. *Synthesis* **1988**, 943.

(12) Lin, T. S.; Luo, M. Z.; Liu, M. C. *Tetrahedron Lett.* **1994**, *35*, 3477.

(13) **Typical Procedure for the Catalytic Reaction.** In a typical experiment the diselenide (**1**) (18.6 mg, 0.02 mmol) was placed in a three-necked round-bottom flask carrying a sidearm addition tube containing $NaBH_4$ (7.4 mg, 0.2 mmol). Deoxygenated ethanol (1 mL) was added, and the mixture was cooled to 0 °C under an Ar atmosphere. The $NaBH_4$ was then added slowly (H_2 evolution) until the orange solution turned colorless. After 1 h the dimesylate **2** (41 mg, 0.1 mmol) dissolved in THF (1 mL) was added, and the reaction mixture was heated to reflux for a period of 5−6 h. After cooling to room temperature, the reaction mixture was diluted with CH_2Cl_2 (5 mL), washed with water, and concentrated in vacuo. The extracts were taken up again in CH_2Cl_2 (5 mL) and partitioned with FC 72 (15 mL) in the continuous extractor[4] for 2 h. The fluorous diselenide (**1**) was recovered by evaporation of the FC 72 phase (14.1 mg, 76%) and the olefin (**3**) by flash chromatography over silica gel using 25% EtOAc−hexane as eluent (31 mg, 74%).



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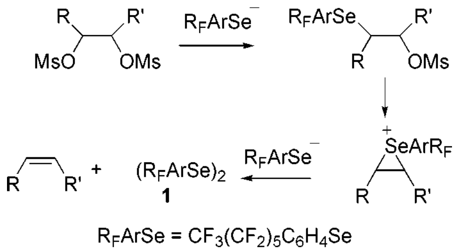
an acceptable level (Table 1). Attention is also directed to the dimesylates **4** and **6** leading to the hydrocarbons **5** and **7**, respectively; the use of the fluorous diselenide **1** and fluorous extraction greatly facilitated the separation of these hydrocarbons from the very nonpolar diselenides.

Like Clive,[1,2] we propose that these reactions proceed by S_N2 displacement of a first mesylate by the areneselenide anion, followed by closure to give a cyclic episelenenium ion, and final selenophilic attack by the second equivalent of selenide anion to liberate the product and regenerate the catalyst (Scheme 1). Also like Clive,[1] we find similar constraints imposed by steric hindrance; thus 2-*exo*-3-*exo*-camphanediol dimesylate was not a substrate for the present nor the original reaction, being recovered unchanged.

Scheme 1. Proposed Mechanism for Elimination



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