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Ru(bpy)$_3$$^{2+}$-Mediated Addition of *Se*-Phenyl p-Tolueneselenosulfonate to Electron Rich Olefins

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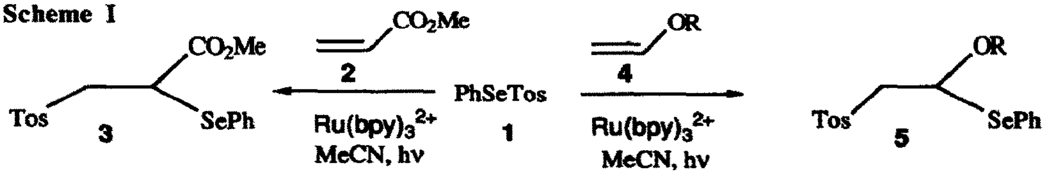
Abstract: The addition of Se-phenyl p-tolueneselenosulfonate 1 to electron rich olefins 4a-4e upon visible light photolysis with a catalytic amount of tris(2,2'-bipyridine)ruthenium(II) gives adducts 5 in high yield.

The addition of various phenylselenenyl compounds to unsaturated systems is a well-documented reaction in synthetic organic chemistry.[1,2] These reactions can be both ionic and radical processes and because of their usefulness, have received much-deserved interest recently.[3] It has been established that Se-phenyl areneselenosulfonates add to various olefins in Lewis acid catalyzed ionic, as well as thermally initiated radical reactions.[3,4] The two reactions have opposite regiochemical outcome, allowing, after oxidation and syn-elimination, the synthesis of the two possible substituted olefin regioisomers.[5,6]

We envisioned, that catalytic amounts of tris(2,2'-bipyridine)ruthenium(II)[7] could initiate this addition reaction upon photolysis. This would then also allow the use of this ruthenium complex with visible light for various other radical reactions. The catalyst, Ru(bpy)$_3$$^{2+}$ is known to act as an electron transfer agent in its photochemically excited, first triplet charge transfer state.[8,9] Consequently, we assumed, that this system could be used as a SET initiator in the attempted addition reaction between Se-phenyl selenosulfonates and various unsaturated compounds, including vinyl-ether type electron rich olefins. This would also allow other applications of the Ru(bpy)$_3$$^{2+}$/visible light system as an initiator in radical chemistry.

Visible light photolysis with a 1 million candlepower xenon lamp[10] of Se-phenyl p-tolueneselenosulfonate[11] 1 (1 equiv.) with 10 equivalents of an electron-deficient olefin, methyl acrylate 2 without the ruthenium catalyst gave mainly the polymer with the formation of some addition product. The same experiment, in the presence of a relatively large amount (10%) of Ru(bpy)$_3$$^{2+}$ gave a much cleaner reaction mixture and the yield of the adduct 3 was 84% (**Scheme I**).

Scheme I



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§This publication is dedicated to Professor M. T. Beck (Institute of Physical Chemistry, Kossuth Lajos University of Arts and Sciences, Debrecen, Hungary) on the occasion of his 65th birthday.

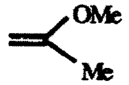
The use of electron-rich olefins of vinyl ether type **4**, gave a high yielding addition reaction of Se-phenyl p-toluenesulfonylselenosulfonate in a range of $Ru(bpy)_3^{2+}$ concentrations (0.2-10 %). The reaction furnished selenoethers **5** in (80)-90-95% yield (^1H NMR)[12] (**Table 1**).[13]

Table 1 Synthesis of selenoethers **5a-e** from vinyl ethers **4a-e**.

Product **5**	R	Yield[a] (%)	IR (cm^{-1}) (film)		^{13}C NMR (δ, ppm) ($CDCl_3$)
5a	ethyl	90 (75)[b]	1580 1340	1450 1150	145.0, 137.8, 136.5, 129.7 129.0, 128.5, 126.5, 78.9, 66.0, 64.2, 22.1, 14.6
5b	n-butyl	92	1602 1330	1472 1150	144.5, 137.1, 136.0, 129.6, 129.2, 128.5, 127.9, 126.3, 78.5, 70.0, 63.5, 30.8, 21.5, 19.1, 13.8
5c	i-butyl	93	1600 1340	1465 1137	144.9, 137.8, 136.5, 130.1, 129.7, 129.0, 128.4, 126.0, 79.2, 77.5, 64.1, 28.4, 22.0, 19.8, 19.7.
5d[c]	$(CH_2)_2$	90	1596 1310	1423 1144	145.3, 134.9, 130.2, 129.2, 128.7, 128.3, 82.3, 70.9, 67.6, 26.2, 21.8
5e[d]	Me[e]	80	n.a.[f]		144.1, 136.4, 129.4, 129.1, 128.7, 128.1 128.1, 88.3, 66.8, 51.9, 24.4, 21.7

[a] Determined by 1H NMR. [b] Isolated.

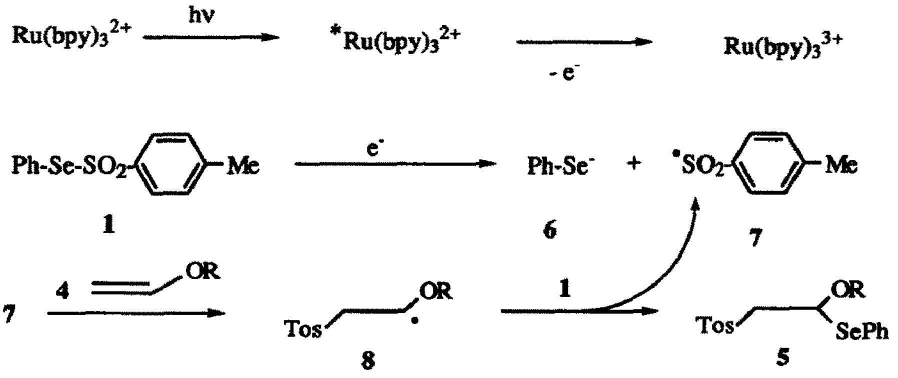
[c] From  [d] The product is 

[e] From 

[f] Not available.

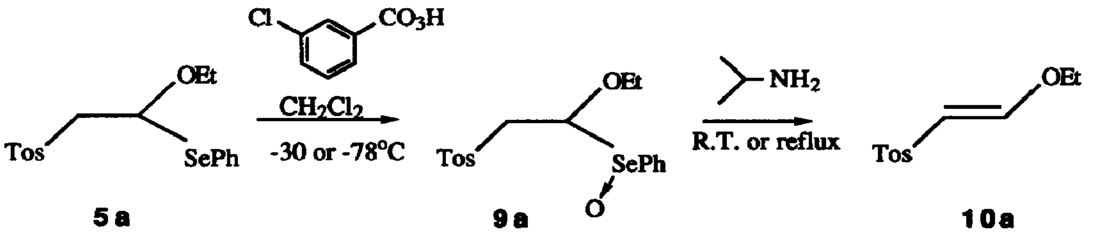
The proposed mechanism of the reaction is shown on **Scheme II**.

Scheme II



The regiochemistry of the addition reaction can be proven by chemical methods and also by NMR techniques. Thus, adduct **5a** was oxidized to the corresponding selenoxide **9a** with m-chloroperoxybenzoic acid in methylene chloride at -30°C or at -78°C. The selenoxide, thus formed, underwent syn-elimination upon warm-up in the presence of isopropylamine and the 1,2-disubstituted trans olefin **10a** was isolated by flash column chromatography on silica (ethyl acetate: hexanes = 1:4) in 76-80% yield (**Scheme III**). The ^3J = 12.3 Hz coupling constant between the olefinic protons is characteristic and excludes the possibility of the other regioisomer selenoether. ^{13}C NMR measurements also reveal Se-related satellites of a C-H carbon, indicating again that the regioisomer obtained in the addition is of type **5**. This regiochemistry was observed in the radical azido-phenylselenenylation of vinyl ether type compounds and glycals.[14,15]

Scheme III



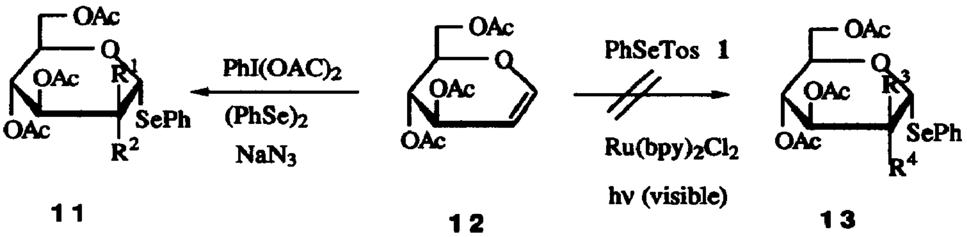
We have studied the influence of reaction temperature on the yield of the isobutyl compound **5c**. Thus, 0.1 mmole of Se-phenyl p-tolueneselenosulfonate **1** and 10 mmole of isobutyl vinyl ether **4c** were dissolved with 0.5 mol % $Ru(bpy)_3Cl_2$ in 4 ml of degassed acetonitrile. The solution was irradiated with a 1 million candlepower xenon lamp for 10 min. and the solvent was removed in vacuum. The yield, determined by ^1H NMR was 95% at 0°C, decreased slightly to 85% at -20°C. When the reaction was carried out at -40°C, 82% of **5c** was measured.

The effect of the ratio of the two reagents was also studied. Thus, when the olefin **4c** was used in a tenfold excess, the yield of **5c** was 95%. When the reaction was carried out with 1 equivalent olefin at -10°C, the yield was somwhat lower (83%).

We have studied the effect of other ruthenium complexes on this selenosulfonation reaction. $Ru(CO)_3Cl_2$ behaved similarly giving 86% of **5c** from **4c**. $Ru(PPh)_3Cl_2$ furnished the desired adduct **5c** too, but a lot of the olefin **4c** was polymerized in this reaction.

It is known, that glycals undergo free-radical addition reaction of phenylselenenyl azide[15] that result in the formation of 2-azido-2-deoxy-1-selenoglycosides **11**. Selenoglycosides are useful as glycosyl donors in various glycosylation reactions. Consequently we have attempted to react 3,4,6-tri-*O*-acetyl-D-glucal **12** with *Se*-phenyl selenotosylate **1** (**Scheme IV**).

Scheme IV



However, our system with a catalytic amount of $Ru(bpy)_3Cl_2$ and visible light photolysis failed to give the corresponding phenylselenyl derivative **13** from glucal. It remained unchanged, or only the decomposition of the glucal **12** was observed. This is an indication that the p-toluenesulfonyl radical **7** did not react with **12**.

Isolation of diphenyl diselenide from the **4a** to **5a** reaction mixture allows us to estimate the length of the radical chains. Assuming that the Ru^{III} is reduced back to Ru^{II} by $PhSe^-$ and that all the phenylselenyl radicals are dimerised to $(PhSe)_2$ then the amount of diphenyl diselenide indicates that the radical chain length is about 50 in this case. The proposed mechanism and the scope and limitations of this reaction is under further study.

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REFERENCES AND NOTES:

1 Paulmier, C. *Selenium Reagents and Intermediates in Organic Synthesis;* Organic Chemistry Series (Baldwin, J. E., Ser. Ed.) Pergamon Press, Oxford, 1986.

2 *Organoselenium Chemistry,* (Liotta, D., Ed.); Wiley-Interscience, New York, 1987.

3 Back, T. G. Ref. 2, Chapter 1, pp. 56-95.

4 Back, T. G.; Collins, S. *Tetrahedron Lett.* **1980**, *21*, 2215.
Idem, *J. Org. Chem.* **1981**, *46*, 3249.

5 Ref. 1, Chapter VII, pp. 182-227.

6. Kang, Y.-H.; Kice, J. L. *Tetrahedron Lett.* **1982**, *23*, 5373.

7 Burstall, F. H. *J. Chem. Soc.* **1936**, 173.

8 Gafney, H. D.; Adamson, A. W. *J. Am. Chem. Soc.* **1972**, *94*, 8238.

9 Bock, C. R.; Meyer, T. J.; Whitten, D. G. *ibid.* **1974**, *96*, 4710.
Joo, F.; Csuhai, E.; Quinn, P.; Vigh, L. *J. Mol. Catal.* **1988**, *49*, L1.
Chanon, M. *Acc. Chem. Res.* **1987**, 20, 214.
Juilliard, M.; Chanon, M. *Chem. Rev.* **1983**, 83, 425.
Okada, K.; Okubo, K.; Morita, N.; Oda, M. *Chem. Lett.* **1993**, 2021.

10 Barton, D. H. R.; Tang, D.; Jaszberenyi, J. Cs. *Tetrahedron Lett.* **1993**, *34*, 2311

11 Barton, D. H. R.; Britten-Kelly, M. R.; Ferreira, D. *J. Chem. Soc. Perkin I*, **1979**, 2661.
Back, T. G.; Collins, S. *Tetrahedron Lett.* **1980**, *21*, 2213.

12 ^1H NMR (200 MHz, $CDCl_3$, d): **5a**: 7.7 (d, 2H), 7.5 (dd, 2H), 7.25 (m, 5H), 5.35 (dd, 1H), 3.85 (dd, 1H), 3.6 (m, 2H), 3.35 (dd, 1H), 2.4 (s, 3H), 1.0 (t, 3H). **5b**: 7.7 (d, 2H), 7.5 (dd, 2H), 7.3 (m, 5H), 5.35 (dd, 1H), 3.8 (m, 1H), 3.65 (s, 1H), 3.62 (d,1H), 3.25 (m, 1H), 2.4 (s, 3H), 1.25 (m, 4H), 0.85 (t, 3H). **5c**: 7.7 (d, 2H), 7.5 (d, 2H), 7.3 (m, 5H), 5.3 (dd, 1H), 3.6 (m, 3H), 3.05 (dd, 1H), 2.4 (s, 3H), 1.6 (m, 1H), 0.75 (t, 6H). **5d**: 7.7 (d, 2H), 7.45 (dd, 2H), 7.3 (m, 5H), 6.1 (d, 1H), 4.05 (m, 2H), 3.85 (m, 1H), 2.45 (m, 3H), 2.35 (m, 2H). **5e**: 7.55 (d, 2H), 7.3 (d, 2H), 7.2 (m, 5H), 3.62 (s, 1H), 3.6 (s, 1H), 3.22 (s, 3H), 2.4 (s, 3H), 1.89 (s, 3H).

13 Satisfactory microanalysis data were obtained for the adducts **5a-e**.

14 Tingoli, M.; Tiecco, M.; Chianelli, D.; Balducci, R., Tamperini, A. *J. Org. Chem.* **1991**, *56*, 6809.

15 Santoyo-Gonzâlez, F.; Calvo-Flores, F. G.; Garcia-Mendoza, P.; Hernândez-Mateo, F.; Isac-Garcia, J.; Robles-Diaz, R. *ibid.* **1993**, *58*, 6122.

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