

Photosensitized One-electron Reductive Cleavage of a Carbon–Selenium Bond: a Novel Chemoselective Deselenenylation and Phenylselenenyl Group Transfer Radical Chain Reaction

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A novel photosensitized one-electron reduction of organoselenium compounds leading to chemoselective deselenenylation and phenylselenenyl group transfer radical chain processes is reported.

The study of mechanistic and synthetic problems pertaining to the chemistry of photoinduced electron transfer (PET) generated radical ions has witnessed growing importance during the last decade.^{1,2} The efficient fragmentation of radical ion to charged species and neutral radicals, simultaneously, has provided organic chemists with a unique opportunity to exploit these intermediates in various synthetic reactions.³ A recent investigation from our group has elucidated⁴ the PET oxidation of organoselenium compounds and the results have suggested their possible utilization as carbocation equivalents in addition to their normal use as carbanion and free radical equivalent.⁵ However, the mechanistic and synthetic perspectives of such compounds by one-electron photoreduction has remained unexplored. In this communication we report an unprecedented PET reduction phenomenon from organoselenium substrates employing photoexcited 1,5-dimethoxynaphthalene (DMN*) as electron donor. This study is of mechanistic interest and has also provided a novel approach for a chemoselective deselenenylation reaction and phenylselenenyl group transfer radical chain reaction.

From recent studies^{6,7} it is apparent that photoexcited electron rich aromatics, particularly DMN* ($E_{1\text{ox}} = 1.28$ eV,

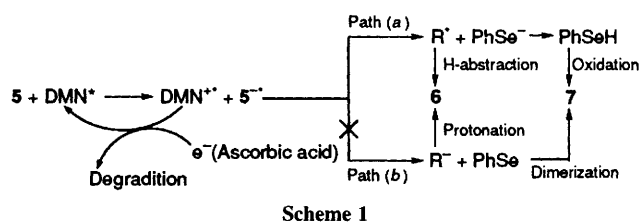
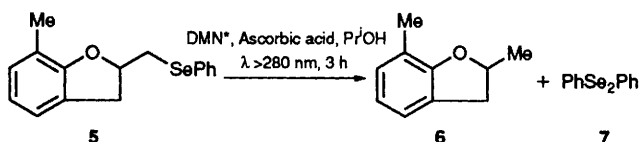
$E_{0,0} = 87.8$ kcal mol⁻¹),⁶ are effective electron donors. Therefore, we elected to use DMN* as a possible electron donor to organoselenium compounds. In this context, the feasibility of electron transfer (ET) was established by estimating the endoergic (negative) free energy change ($\Delta G_{\text{ET}} = 35\text{--}44$ kcal mol⁻¹) between DMN* and organoselenium compounds 1–4 ($E_{1\text{red}} = 0.60\text{--}1.00$ eV)[‡] by using the well known Weller equation.⁹ Further support for this phenomenon is obtained from a linear Stern–Volmer quenching analysis of DMN fluorescence by 1–4 which has indicated the quenching rate constant (K_{qET}) to near diffusion.[§] Emission and absorption spectroscopic properties of 1–4 and DMN in polar as well as non-polar solvents fail to suggest ground or excited state complexation. Therefore, it is reasonable to assume that fluorescence quenching involves ET *via* a

Table 1 Photophysical constants evaluated for PET from DMN to organoselenium substrates

Substrate	$E_{1\text{red}}^a/eV$ (vs. SCE)	$\Delta G_{\text{ET}}^b/\text{kcal mol}^{-1}$	$10^{-10}K_{\text{qET}}^c/\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$
PhCH ₂ SeCH ₂ Ph 1	-0.60	-44.14	0.611 ± 0.002
PhSeC ₂ H ₅ 2	-0.70	-42.14	0.368 ± 0.001
PhSeC ₈ H ₁₇ 3	-0.80	-39.83	0.303 ± 0.005
C ₄ H ₉ SeC ₄ H ₉ 4	-1.00	-35.22	0.184 ± 0.003

^a Measured by cyclic voltametry (*cf.* ref. 8). ^b ΔG_{ET} is estimated by taking DMN oxidative half wave potential ($E_{1\text{ox}} = 1.28$ eV and $E_{0,0} = 87.8$ kcal mol⁻¹) (*cf.* ref. 6).

[‡] The reduction potentials were measured from cyclic voltametry using a three electrode assembly with a PAR 175 universal programmer and PAR RE 0074 XY recorder. The cell consisted of a Metro E410 hanging mercury drop electrode (HMDE) and Pt wire (auxiliary electrode), the supporting electrolyte was tetraethylammonium perchlorate and potentials are referred to SCE and are uncorrected for liquid junction potential. Identical conditions are also used by Atsutaka *et al.* for determining the electrode potential of diselenides.⁸

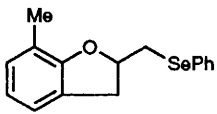
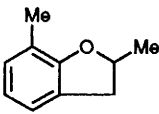
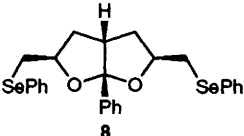
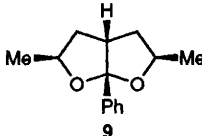
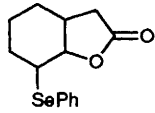
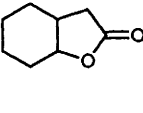
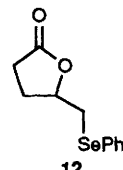
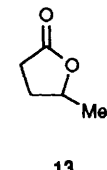
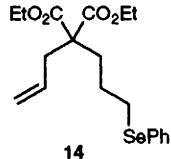
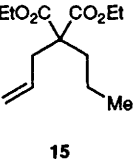


Scheme 1

† NCL Communication No. 5781.

§ The singlet life time of DMN was taken as 12.6 ns (*cf.* ref. 6).

Table 2 Photosensitized chemoselective deselenenylation of organoselenium substrates

Substrate	Product ^a	t/h	Yield ^b (%)	ϕ_{disapp}^c
		3	90	0.0114 ± 0.0001
		3	85	0.0089 ± 0.0011
		3.5	89	0.0090 ± 0.0001
		3	83	0.0098 ± 0.0006
		4	80	0.0091 ± 0.0004

^a Characterized by ¹H and ¹³C NMR and MS data. ^b Isolated yields but not optimized; yields are calculated by extrapolating 100% transformation of substrate to product. ^c Light intensity ($\lambda = 300$ nm) evaluated by uranyl oxalate actinometer.

charge-transfer stabilized exciplex. A convincing proof of this effect is provided by a linear correlation plot of $\log[K_{\text{qET}}]$ vs. E_3 red of 1–4. The details of photophysical constants are given in Table 1.

The above photophysical observation encouraged us to carry out a photosensitized ET reaction from organoselenium compounds in the presence of DMN*. Compound **5** (1.6 mmol) was irradiated ($\lambda > 280$ nm, Pyrex filter, 450-W Hanovia medium pressure mercury lamp) in isopropanol containing DMN (1.6 mmol, all light absorbed by DMN only) and ascorbic acid (as co-reductant,⁶ 1.6 mmol) for 3 h; without removing dissolved oxygen from the reaction mixture, to give **6** and **7** along with quantitative recovery of DMN (98%) upon work-up and purification (Scheme 1). Photoreaction of **5** without DMN failed to show any reaction, suggesting the sensitized role of DMN.

Mechanistically the reaction may be rationalized by considering the initial one-electron transfer from DMN* to **5** and the steps as shown in Scheme 1. The regeneration of DMN by ascorbic acid is preceded from a literature report.⁶ The cleavage of **5**^{•-} by path (b) is ruled out by performing an analogous photoreaction in deuterated isopropanol (PrⁱOD) which failed to indicate any deuterium incorporation in product **6** (monitored by ¹H NMR and MS). It is therefore, possible to consider the cleavage of **5**^{•-} by path (a). The well known¹⁰ instability of phenylselenol (PhSeH) leads to the formation of **7** via a dimerisation reaction.

Since chemoselective deselenylation is an important aspect of synthetic manipulations using organoselenium reagents, a milder and effective approach for this purpose is always desirable. Among the reductive deselenylation processes,¹¹

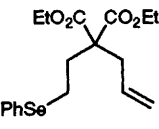
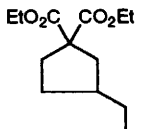
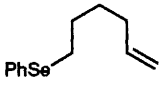
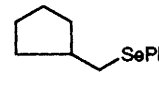
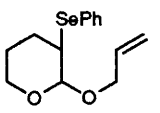
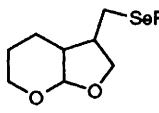
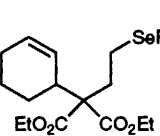
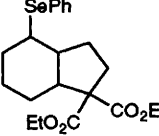
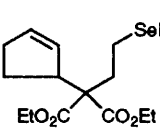
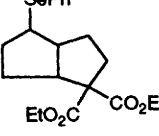
tributyltin hydride^{11a} mediated reduction is considered selective, however, owing to its inherent limitations, a selective deselenylation reaction is required. Thus the exploitation of the present photochemical approach can be considered as an attractive alternative to effect selective deselenylation. Examples listed in Table 2 show the generality and potential of this methodology.

Further, to substantiate the cleavage of **5**^{•-} by path (a) (Scheme 1) and to expand the utility of this reaction, we envisioned that the PET reaction from organoselenium compounds containing a proximate π -bond (e.g. **16**) in non-hydrogen donating solvents would lead to the formation of **17** through the radical chain sequences. Identical irradiation of a mixture containing **16** (1.3 mmol), DMN (0.65 mmol), and ascorbic acid (0.65 mmol) in MeCN–H₂O (4:1); without removing dissolved oxygen from the solution, until 70% consumption of **16** (ca. 10 h, ¶ monitored by HPLC, C₁₈ reversed-phase column) and usual work-up followed by purification through column chromatography furnished cyclized product **17** in 88% yield, characterized by ¹H, ¹³C NMR and MS data. This reaction gave only trace amount of *endo*-trig cyclization product.

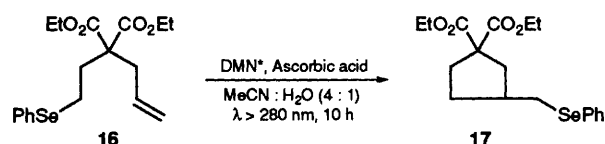
Since it is obvious that there will not be quantitative transformation of **16** to **17** due to the time lag for the accumulation of **7** required for the termination of the radical chain process, the quantum efficiencies for the ϕ_{disapp} of **16** (0.0087) and ϕ_{app} of **17** (0.0077) were compared and a

¶ The longer irradiation time for **16** → **17** may be due to the solvent polarity and the difference in the terminating step of radical species when compared with the formation of **15**.

Table 3 Photosensitized phenylselenenyl group transfer radical chain reaction

Substrate	Product ^a	<i>t</i> ^b /h	Yield ^c (%)
		10	88
		10	80
		9	85
		10	84
		10	80

^a Characterized by ¹H and ¹³C NMR and MS data. ^b Irradiated until 70% consumption of substrate. ^c Isolated yields but not optimized; calculated based on the consumption of substrate.



difference of 11.45% was observed, which indicates that only 11.45% of **16** is unaccounted in this reaction. We have found that complete conversion of **16** to **17** can be achieved by

performing the photoreaction containing trace amount of **7** in the initial reaction mixture.

As shown in Table 3, a variety of typical radical reactions can be performed using this novel methodology.

In conclusion, we have demonstrated a mechanistically new photosensitized reaction useful for chemoselective deselenylation reaction, and to propagate radical chain reactions which circumvents the drawbacks of tributyltin hydride mediated radical chain processes.¹²

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