Photoinduced Electron Transfer Initiated Activation of Organoselenium Substrates as Carbocation Equivalents: Sequential One-Pot Selenylation and Deselenylation Reaction[†]

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The investigation presented in this paper explores the mechanistic aspects and synthetic potentials of PET activation of organoselenium substrates. Fluorescence quenching of $^1DCN^*$ by a number of organoselenium compounds (RCH_2SeR', **1–4**), correlation of the fluorescence quenching rate constants with the oxidation potentials of **1–4**, and the dependence of photodissociation quantum yields of **1–4** on their concentration suggests the occurrence of electron transfer processes between $^1DCN^*$ and **1–4**. Steady-state photolysis of **1–4** in the presence of $^1DCN^*$ leads to the efficient one-electron oxidative heterolytic dissociation of the carbon–selenium bond to produce the carbocation (RCH_2^+ or equivalent) and radical-centered selenium species ($R'Se^•$) *via* the intermediacy of cation–radical [$(RCH_2SeR')^{+•}$]. Nucleophilic assistance in the fragmentation of ($RCH_2SeR')^{+•}$ by methanol has been suggested on the basis of products obtained from the control PET reaction of neopentyl phenyl selenide (**8**). The synthetic utility of these findings has been demonstrated for the deselenylation (Table 4) as well as one-spot sequential selenylation–deselenylation (Table 5) reactions.

Introduction

Photoinduced electron transfer (PET) reactions have been the topic of recent investigations leading to the discovery of several new synthetically useful chemical reactions.[1,2] The novelty of these transformations is associated with the facile generation of potentially reactive radical ions from a neutral molecule rather than the initially populated excited states, as happens in the case of normal photochemical reactions.[3,4] The nature of PET initiated reactions, is, therefore, governed by the chemical properties and reactivity profiles of the ion–radicals. These ion–radicals undergo predominant disproportionation into charged and/or neutral species which are the key reactive intermediates in organic synthesis.[5,6]

A vast majority of reactions in this area have focused attention on the chemistry originating from the cation–radical species owing to their enhanced acidity and efficient cleavage of the relatively weaker bonds with the consequent formation of a radical and cationic species with the lifetimes and chemical affinities different from the parent species.[7,8] The most common reaction ob-

served from these intermediates has been the loss of electrofugal group (H+ [1b,c,9] or metal cations such as $-MR_3^+$;[1b,10] M = Pb, Si, Sn, Ge) from the sites adjacent to the charged radical center. Fragmentation of M–M]+• has also been reported from Group 14 dimetallic compounds.[11,12] Analogous cleavage of diphenyl diselenide (PhSeSePh) *via* PhSeSePh]+• to electrophilic selenium species (PhSe+) has been reported[13] from our group by the "true photosensitized" reaction utilizing the singlet excited state of 1,4-dicyanonaphthalene (DCN) as an electron acceptor. As part of our continuing interest in this area, we elected to explore the consequences of PET processes and their synthetic potentials from the compounds containing a carbon–selenium (>C–Se–) bond with the intention of unravelling the mode of fragmentation of the resultant (>C–Se–)+• intermediate to produce either the carbon centered radical (>C•) or the carbocation (>C+). In this paper, we present the full details of our preliminary studies[14] on the PET initiated cleavage of

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Table 1. Physical Constants Evaluated for PET from Organoselenium Substrates 1–4

selenide[a]	K_{qf}[b] $(10^{10}$ M^{-1} s$^{-1})$	K_{qET}[c] $(10^{10}$ M^{-1} s$^{-1})$	$E_{1/2}^{ox}$[d] (eV)	ΔG_{ET}[e]	Φ_{disap}[f]	Φ_{lim}[f,g]
1	1.92 ± 0.07	1.59 ± 0.05	1.35	−18.90	0.012 ± 0.001	0.054 ± 0.002
2	0.44 ± 0.03	0.26 ± 0.02	1.62	−12.66	0.021 ± 0.002	0.172 ± 0.007
3	0.54 ± 0.02	0.54 ± 0.04	1.60	−13.08	0.023 ± 0.002	0.121 ± 0.005
4	0.47 ± 0.04	0.59 ± 0.04	1.65	−11.99	0.015 ± 0.001	0.141 ± 0.006

[a] Errors are standard deviations from the average. [b] From fluorescence quenching Stern–Volmer plot. [c] From reciprocal plot; $(\phi_{disap})^{-1}$ *vs* $[1–4]^{-1}$. [d] Referred to saturated calomel electrode (SCE) using tetraethylammonium perchlorate as supporting electrolyte in dry acetonitrile. [e] ΔG_{ET} expressed in kcal/mol; reduction half-wave potential for DCN $(E_{1/2}^{red} = -1.28$ eV) and $E_{0,0} = 3.45$ eV. [f] Light intensity was evaluated by uranyloxalate actinometry; for details see Experimental Section. [g] At infinite donor concentration; measured from the plot of $(\phi_{disap})^{-1}$ *vs* $[1–4]^{-1}$.

Table 2. Product Composition in Photolysis Mixture of Selenides 1–4

	product composition in MeOH (%)				
	ether (**5**)/yield		diselenide (**6**)/yield		
selenide	ether[b] (**5**)	yield[c] (%)	diselenide[b] (**6**)	yield[c] (%)	others[d]
1[e]			PhSeSePh		
2	n-C$_8$H$_{17}$OMe	61.4	PhSeSePh	38.3	
3	PhCH$_2$OMe	73	(PhCH$_2$Se–)$_2$	18	PhCH$_2$CH$_2$Ph (**5**)[f] Se metal
4	n-C$_4$H$_9$OMe	76.4	(n-C$_4$H$_9$Se–)$_2$	23.2	

[a] Characterized by identical GC (column: 8 ft × 1/8 in., 10% OV-17) retention times when coinjected with authentic compounds and with GC–MS (column: methyl silicone, capillary). [b] The products mentioned are primary photoproducts confirmed by irradiating for short period. [c] GC yields calculated after correcting detector response factors. [d] The products mentioned are the secondary products. [e] Reaction product ether (C$_2$H$_5$OMe) could not be isolated, due to low boiling point. [f] Number in parentheses is GC yield.

the >C–Se– bond possessing organoselenium substrates using ^{1}DCN* as an electron acceptor. The results suggest the utilization of >C–Se– bond as a carbocation equivalent in addition to its well known use as a carbanion and radical equivalent.[15] Steady state analysis of the fluorescence quenching, the dependence of >C–Se– bond cleavage quantum yield on quencher concentration, nucleophilic trapping of the resultant carbocationic species, and novel deselenylation strategy provides the complete dissection of the PET phenomenon from these systems.

Results and Discussion

The fluorescence quenching of DCN ($\lambda_{ex} = 320$ nm, $\lambda_{em} = 391$ nm) by organoselenium compounds **1–4** obeys the Stern–Volmer relation (Figure 1, supplementary material). From the slopes ($K_{qf}\tau$) of the straight lines (Figure 1), taking $\tau = 10.1$ ns,[16] the quenching rate constants (K_{qf}) were calculated (correlation coefficient > 0.99, SD = 0.045) and were found to be close to the diffusion controlled limit[1c] ($K_{diff} = 2.30 \times 10^{10}$ M^{-1} s^{-1}, Table 1). Excitation and absorption spectra of DCN were unaffected in the presence of the maximum concentration of **1–4**. The quenching, therefore, cannot be attributed to the ground state complexation between the DCN and **1–4**. No exciplex emission was noticed either in polar or nonpolar solvents. Fluorescence quenching due to the exothermic singlet energy transfer from the excited DCN ($E_S = 79.5$ kcal/mol)[1c] to **1–4** has been ruled out simply on considering the energetics. Quenching due to the

heavy atom induced intersystem crossing could also suggest to be minimal based on the similar pattern as reported by Eaton et al.[10c] It is, therefore, reasonable to assume that fluorescence quenching in these cases occurs *via* the single electron transfer (SET) mechanism involving the charge transfer (CT) stabilized exciplex. This is further supported by the estimation of the free energy change (ΔG_{ET}) associated with the SET phenomenon by the Weller equation (eq 1),[17] where $E_{1/2}^{ox}$[D] is the

$$\Delta G_{ET} = E_{1/2}^{ox}[D] - E_{1/2}^{red}[A] - E_{0,0} \qquad (1)$$

oxidation potential of the donors **1–4**, $E_{1/2}^{red}$[A] is the reduction potential of the acceptor (DCN), and $E_{0,0}$ is the singlet energy of the excited species (DCN). Substitution of eq 1 with the appropriate values of the oxidation potentials of **1–4**, obtained by cyclic voltammetry (*cf.* for details see Experimental Section), reduction potential (−1.28 eV),[1c] and excitation energy (3.45 eV)[1c] of DCN, respectively, gave exergonic (negative) values for all the compounds (Table 1). The SET mechanism for the fluorescence quenching of DCN by **1–4** is further supported from a linear relationship (Figure 2, supplementary material) through the correlation plot of log[K_{qf}] *vs* $E_{1/2}^{ox}$ of **1–4**.

PET reaction from a donor–acceptor pair results in the formation of radical ions in competition with the back-electron transfer.[3,4] The reactivities of these radical ions are governed, among many other factors, by the solvent polarity. A closely related question is whether the primary intermediate is a solvent separated ion pair (SSIP) or contact ion pair (CIP). Gould and Farid,[18] in their recent study, have suggested that in polar solvents, the electron transfer quenching results in the formation of SSIP directly and in these solvents the fully solvated ions can separate to form free radical ion pairs (FRIP). In polar solvents, the anion radicals are potentially less reactive with the cation radicals than in the nonpolar solvents in which the CIP is important.[19] Under this premise and on the basis of the above photophysical correlation for the electron transfer reaction between ^{1}DCN* and **1–4**, it was envisioned that the PET reaction from these mixtures in polar solvents will lead to the chemistry predominantly from the cation radicals of **1–4**. To this end, a mixture containing **1–4** (3.0 mM) and DCN (0.3 mM) in methanol was irradiated by the Pyrex filtered light ($\lambda > 280$ nm, all light absorbed by DCN only) using a 450-W Hanovia medium-pressure mercury vapor lamp, without removing the dissolved oxygen from reaction mixture. Analysis of the reaction mixture indicated the

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Scheme 1

$$R-CH_2-Se-R'$$

1-4

$\downarrow$ $^1DCN^*$ / MeOH

Path b $\times$ $\left[R-CH_2-Se-R'\right]^{+\bullet}$ Path a

$R'Se^+ \leftarrow$ $\rightarrow R'\overset{\bullet}{Se} \longrightarrow R'SeSeR'$

6

$\rightarrow R-\overset{\bullet}{C}H_2 \overset{-e}{\longrightarrow} R-\overset{+}{C}H_2 \overset{MeOH}{\longleftarrow} R-CH_2-OMe$

5

1   R = CH$_3$, R' = Ph

2   R = n-C$_7$H$_{15}$, R' = Ph

3   R = Ph , R' = PhCH$_2$

4   R = n-C$_3$H$_7$, R' = n-C$_4$H$_9$
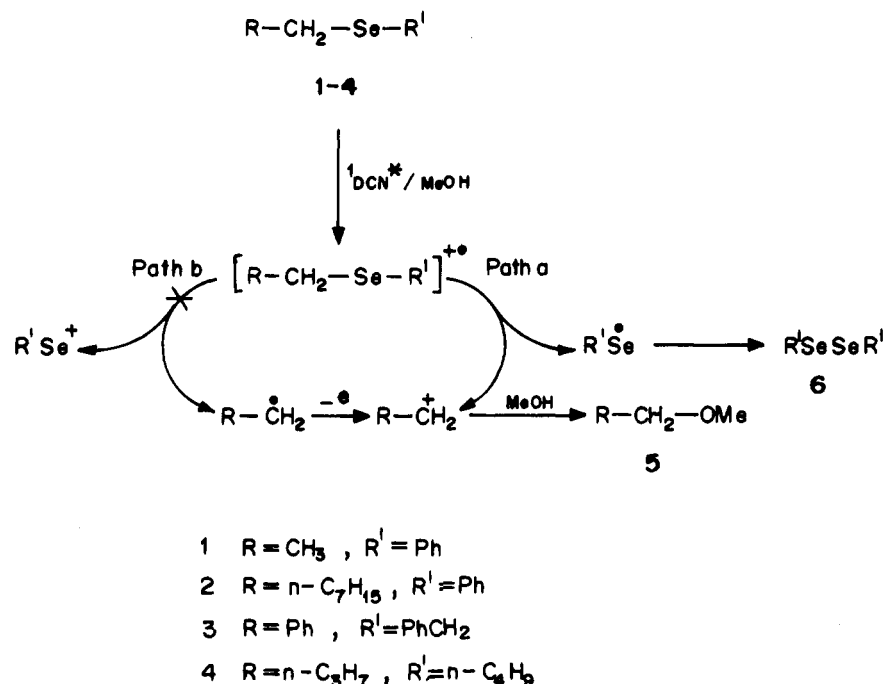
formation of methoxy ethers **5** and diselenylated products **6** in each case as primary products[20] along with the quantitative ($\approx$98%) recovery of DCN. However, the PET cleavage of dibenzyl selenide (**3**) gave bibenzyl and selenium metal in addition to **5** and **6**. The formation of the bibenzyl and selenium metal from the PET reaction of **3** can be explained by considering the secondary fragmentation of initially formed benzylselenyl radical (PhCH$_2$Se$^\bullet$ $\rightarrow$ PhCH$_2^\bullet$ + Se). The formation of only trace amounts of bibenzyl (5%) as compared to the other products supports our argument. Details of the product types, along with their respective yields and the quantum yields disappearance (ϕ_{disap}) from the PET reaction of **1-4**, are given in Table 2.

The formation of **5** and **6** in each case can be suggested by considering the cleavage of PET generated cation radical RCH$_2$SeR']$^{+\bullet}$ as shown in Scheme 1. The generation of the carbon centered radical by following path b can be ruled out on the basis of our failure to trap R'Se$^+$ for selenoetherification reaction from the control experiment designed by irradiating a mixture of **2** (0.5 mM), 5-hexen-1-ol (**7**, 1.0 mM), and DCN (0.5 mM), in an identical manner as reported by us previously.[13] It is, therefore, reasonable to assume that the cleavage of $>$C—Se—]$^{+\bullet}$ species from **1-4** always produces carbocationic species (RCH$_2^+$) and alkyl or aryl selenyl radicals (R'Se$^\bullet$). The carbocationic species, upon trapping with methanol, gave **5**, while selenyl radicals dimerized to produce **6**.

To correlate the photoreaction of **1-4** and the mechanism of DCN fluorescence quenching by **1-4**, it is proposed that an exciplex with the partial charge-transfer character is formed between ^{1}DCN* and **1-4**. A quantitative description of this aspect has been derived by correlating the fluorescence quenching rate constants (K_{qr}) with ϕ_{disap} of **1-4**. A double reciprocal plot of ϕ_{disap} vs concentration of **1-4** [(ϕ_{disap})$^{-1}$ vs [**1-4**]$^{-1}$] resulted a

straight line (Figure 3, supplementary material). The ratio of the intercept/slope ($K_{qET}\tau$) corresponded almost to the identical values (within the acceptable limits of experimental errors) of $K_{q}\tau$ (Table 1) as obtained from the Stern—Volmer fluorescence quenching analysis. The inverse of the intercept gave the limiting quantum yield values (ϕ_{lim}, Table 1) for the disappearance of **1-4**.

The above results can be rationalized with reference to eq 2 to eq 12 (Scheme 2). The photochemical reaction may considered to be initiated by the SET from compounds **1-4** to singlet excited DCN involving CT stabilized exciplex (eq 2). In aqueous methanol, the exciplex is dissociated into SSIP (eq 4) which is further transformed into FRIP (eq 5). There are two possible modes of dissociation of corresponding radical cations from **1-4**. They can either cleave to produce free carbocationic species (eq 7) or may involve the addition of a nucleophile prior to their cleavage (eq 10). Although the addition of a nucleophile to cation radical σ-bonds is much less common,[21] as bond formation between the two reactants requires high activation energy, a recent report has suggested nucleophilic assistance during the cleavage of a stabilized cation radical.[22] To establish the exact mode of cleavage of (RCH$_2$SeR')$^{+\bullet}$, we studied the PET cleavage of neopentyl phenyl selenide (**8**) due to the fact that if free neopentyl carbocation is formed, it will lead to the rearranged product.[23] Irradiation of a mixture of **8** and DCN, in an identical manner as described for **1-4**, gave unrearranged methoxy ether (**9**) as a major product (Scheme 3). This suggests that the fragmentation of **8** does not involve free carbocation and therefore it may be considered that the cleavage of $>$C—Se—]$^{+\bullet}$ is assisted by methanol in the solvent cage (eq 10, Scheme 2), before the rearrangement can occur. This argument is

(20) Formation of **5** and **6** was confirmed by identical GC (column: 8 ft × 1/8 in., 10% OV-17) retention times compared with the identical retention times when the photolysis mixture was coinjected with the authentic compounds and GC–MS (column: 25 mts capillary, methyl silicone) analysis.

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Scheme 2

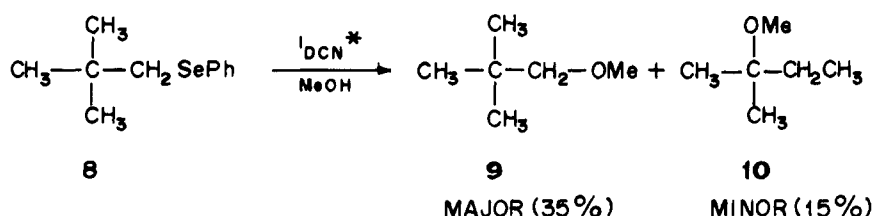$$R-CH_2-Se-R^1 + {}^1DCN^* \longrightarrow \left[(1-4)^{\delta+} --- DCN^{\delta-} \right]^* \text{---------(2)}$$

$$\underset{\textbf{1-4}}{} \qquad\qquad\qquad \underset{\text{exciplex}}{}$$

$$\left[(1-4)^{\delta+} ---- DCN^{\delta-} \right]^* \longrightarrow 1-4 + DCN \text{------------(3)}$$

$$\left[(1-4)^{\delta+} ---- DCN^{\delta-} \right]^* \longrightarrow \left[(1-4)^{+\bullet} \bullet DCN^{-\bullet} \right] \text{------------(4)}$$

$$\qquad\qquad\qquad\qquad\qquad \underset{\text{SSIP}}{}$$

$$\left[(1-4)^{+\bullet} \bullet DCN^{-\bullet} \right] \longrightarrow (1-4)^{+\bullet} + DCN^{-\bullet} \text{----------(5)}$$

$$\qquad\qquad\qquad\qquad \underset{\text{FRIP}}{}$$

$$\left[(1-4)^{+\bullet} \bullet DCN^{-\bullet} \right] \longrightarrow 1-4 + DCN \text{-------------(6)}$$

$$(1-4)^{+\bullet} \longrightarrow R-CH_2^+ + R^1-Se^{\bullet} \text{--------------(7)}$$

$$R-CH_2^+ \xrightarrow{MeOH} 5 \text{-------------------(8)}$$

$$R^1-Se^{\bullet} \longrightarrow 6 \text{----------------------(9)}$$

$$(1-4)^{+\bullet} \longrightarrow \left[R-\underset{HOMe}{\overset{\delta+}{CH_2}}-\overset{\delta-}{Se}-R^1 \right] \longrightarrow 5 + 6 \text{--------(10)}$$

$$DCN^{-\bullet} + O_2 \longrightarrow DCN + O_2^{-\bullet} \text{----------------(11)}$$

$$2H_2O + 2O_2^{-\bullet} \longrightarrow H_2O_2 + O_2 + 2OH^- \text{-----------(12)}$$

Scheme 3

$$\underset{\textbf{8}}{CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH_2SePh} \xrightarrow[MeOH]{{}^1DCN^*} \underset{\textbf{9}}{CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH_2-OMe} + \underset{\textbf{10}}{CH_3-\underset{CH_3}{\overset{OMe}{\underset{|}{\overset{|}{C}}}}-CH_2CH_3}$$

                    MAJOR (35%)   **MINOR (15%)**
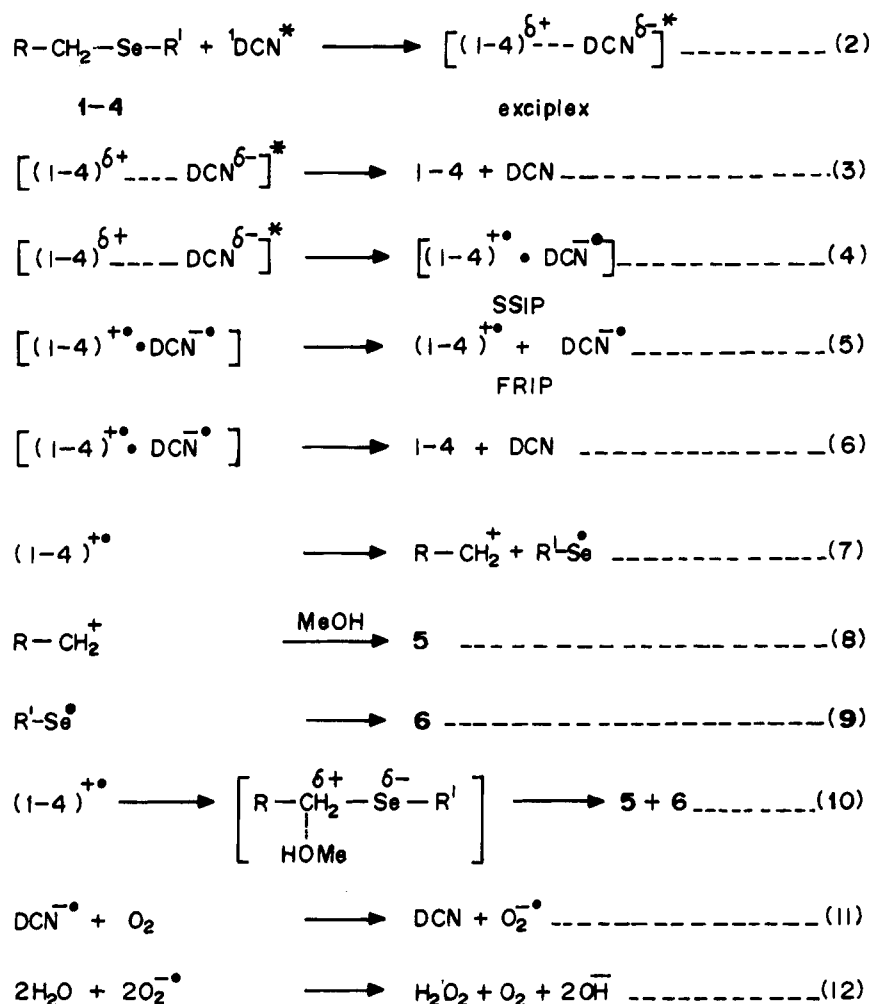
further supported by the absence of rearranged ether products from the PET reaction of **2** and **4**.

The efficient PET cleavage of **1-4** led us to envisage the utilization of >C–Se– bonds as carbocationic equivalents, and hence, we decided to explore the synthetic potentials of fragmentation for the deselenylation reaction. Since deselenylation is an important step after synthetic manipulations using organoselenium reagents, a mild and selective approach for this purpose is always desirable. The existing methodologies for the deselenylation reaction, either by oxidative[24] or reductive[25] processes, suffer from various disadvantages including the loss of functionalities. We therefore envisioned that the PET reaction of organoselenium substrates in methanol

would provide a novel procedure for the deselenylation reaction with the introduction of the methoxy functionality. Identical irradiation of a mixture of **11−16** (4.0 mM) and DCN (0.4 mM) in methanol, as described for **1−4**, resulted in deselenylated products **17−22** in high yields with no side product. Examples listed in Table 3 show the generality of the reaction.

At this point, we reasoned that the combination of our earlier strategy of *in situ* generation of PhSe+ from the PET cleavage of PhSeSePh[13] and the present results may provide a novel methodology for the sequential one-pot selenylation and deselenylation reaction. To this end, usual irradiation of a mixture of **7** (10.0 mM), PhSeSePh (5.0 mM), and DCN (1.0 mM) in methanol led to the formation of **18** as a major product, suggesting the

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Table 3. Deselenylation of Organoselenium Substrates

Entry	Substrate[a]	Product[b]	Irr. time (h)	Yield[c] (%)
1	**11**	**17**	8	70
2	**12**	**18**	8	80
3	**13**	**19**	8	75
4	**14**	**20**	8	73
5	**15**	**21**	8	78[d]
6	**16**	**22a** **22b**	8	72[e]

[a] Preparation and characterization are given in the supplementary material. [b] **17–22** are characterized by IR, ^{1}H NMR, ^{13}C NMR and mass spectra (for **18–20** and **22** see supplementary material). [c] Isolated yields, but not optimized. [d] 7:3 mixture confirmed by ^{13}C NMR; not separable by column chromatography. [e] 2:3 ratio of **22a** and **22b**, respectively, confirmed by GC analysis; stereochemistry not confirmed; characterized by ^{1}H NMR and mass spectra.

success of our concept as outlined at the beginning of this paragraph. Absence of any observable product from a control experiment by identical irradiation of a mixture of **7** (10.0 mM) and DCN (1.0 mM) but without PhSeSePh rules out the possibility of a competitive PET reaction between **7** and ^{1}DCN*. This aspect is further supported by the insignificant fluorescence quenching of ^{1}DCN* by **7**. To test the generality of the one-pot selenylation–deselenylation reaction concept, compounds **23–25** were irradiated and the results are listed in Table 4.

In summary, we have demonstrated the unprecedented PET initiated activation of organoselenium substrates as carbocation equivalents. Application of this concept has led to a novel strategy of deselenylation as well as sequential one-pot selenylation–deselenylation reaction.

Experimental Section

General. DCN[26] and PhSeSePh[27] were synthesized and purified by following the reported procedures. n-C$_8$H$_{17}$OMe, n-C$_4$H$_9$OMe, PhCH$_2$OMe, (CH$_3$)$_3$CH$_2$OMe, and C$_2$H$_5$C(OMe)-(CH$_3$)$_2$ were prepared by the alkylation of respective sodium alcoholates, generated by the treatment of corresponding alcohols with sodium hydride in dry ether, with the methyl iodide. (PhCH$_2$Se–)$_2$[28] and (n-C$_4$H$_9$Se–)$_2$[29] were prepared by following the reported procedures. PhCH$_2$CH$_2$Ph, **7** and **23** were procured commercially from Aldrich Co. Methanol and

Table 4. Sequential One-Pot Selenylation and Deselenylation

Ent.	Substrate[a]	Product[b]	Irr. time (h)	Yield[c] (%)
1	**7**	18	30	70
2	**23**	19	30	67
3	**24**	17	34	65
4	**25**	21	32	72[d]

[a] Preparation and characterization of **24** and **25** are given in the supplementary material. [b] **17–19** and **21** are characterized by IR, ^{1}H NMR, ^{13}C NMR, and mass spectra. [c] Isolated yields, but not optimized. [d] 7:3 mixture confirmed by ^{13}C NMR; not separable by column chromatography.

acetonitrile that were used in HPLC analysis and fluorescence studies, respectively, were of spectroquality (Spectrochem, India) grade. Methanol for the synthesis was purified before use. Silica gel for the column (finer than 200 mesh) and thin layer chromatography was obtained from Acme, India.

All nuclear magnetic resonance spectra were recorded either on Varian FT-80A or Gemini or Bruker 200 spectrometers using CDCl$_3$ as a solvent. All chemical shifts are reported in parts per million down field from TMS; coupling constants are given in hertz. IR spectra were taken on a Perkin-Elmer Model 2830 spectrometer. Mass spectra were obtained at a voltage of 70 eV on Finnigan MAT-1020B instrument. Melting points are uncorrected and were recorded on the centigrade scale in an open capillary on Campbell electronic-thermonic instrument. Elemental analyses were obtained from a CARLO-ERBA CHNS-O EA1108 instrument.

Fluorescence spectra were recorded on a Spex-Fluorolog spectrofluorimeter. The excitation and emission slit widths were maintained at 1.5 mm. The steady state emission spectral measurements were carried out using a 1 cm × 1 cm quartz cell. A right angle configuration for the cell holder was utilized during the measurement of excitation and emission spectra. HPLC analysis was performed on a Shimadzu (LC-6A system along with SPD-6A UV-variable wavelength detector with D$_2$ lamp and C-R3A electronic integrator) liquid chromatograph using reversed phase C$_{18}$ (bondapack 0.5 μm) column, eluting with MeOH:H$_2$O (3:1) solvent mixture degassed by freeze–thaw cycle procedure and monitoring at 254 nm.

Cyclic Voltammetry. The cyclic voltammetry experiments were carried out with a three electrode assembly on a PAR 175 Universal programmer and PAR RE0074 XY recorder. The cell consists of a Metro E410 hanging mercury drop electrode (HMDE) and Pt wire (auxiliary electrode). The supporting electrode was tetraethylammonium perchlorate, and potentials are referred to SCE and are uncorrected for liquid junction potentials.

Fluorescence Quenching. Quenching of DCN fluorescence was carried out by using **1–4** as quenchers. For the determination of Stern–Volmer constants (K_{qf}), the intensity (I_0) of steady state fluorescence at the maximum emission (λ_{em}) 391 nm was measured from a DCN solution (3 × 10^{-4} M) in CH$_3$CN at 25 °C, keeping the excitation wavelength (λ_{em}) at 320 nm. Subsequently, the fluorescence quenching intensity (I) was measured as a function of the concentration [Q] of **1–4**

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in the range of 3×10^{-4} M to 150×10^{-4} M. Linear plots were obtained on the basis of the equation $I_0/I = 1 + K_{q}\tau[Q]$, where I_0 denotes the fluorescence intensity in the absence of quencher. No curvature was noticed in any system and intercepts were 1.00 ± 0.02 in all the cases. Slopes were determined by the least square fit and coefficients were always >0.99.

Quantum Yield Measurements. Samples for the quantum yield determinations were prepared by pipetting out a noted volume from the stock solution of 1–4 into Pyrex tubes and irradiated in a Rayonet reactor using six RUL 3000-Å lamps in a merry-go-round apparatus. Irradiations were carried out for a short interval of time to bring about only 8–10% of the conversion. Uranyl oxalate actinometer was used to monitor the intensity of light.[30] Quantitative loss of the selenides 1–3 was estimated by HPLC [column: C_{18}, eluent; MeOH:H_2O (3:1), UV detector $\lambda = 254$ nm]. Quantitative loss of 4 was estimated by the GC (column: 8 ft × 1/8 in., 10% OV-17) analysis using anisole as an internal standard. The limiting quantum yield (ϕ_{lim}) for each selenide (1–4) was obtained from the inverse plot of the variable donor concentrations (6×10^{-3} M to 27×10^{-3} M) *vs* quantum yields, i.e., $[1-4]^{-1}$ *vs* ϕ_{disap}^{-1}, by keeping the DCN concentration fixed at 3×10^{-4} M.

General Method for the PET Reactions of Selenides 1–4. A mixture containing 1 (0.140 g, 3.0 mM) and DCN (0.013 g, 0.3 mM) in 250 mL of methanol was irradiated at room temperature in a 250 mL irradiation vessel, without removing the dissolved oxygen from the solution, with 450-W Hanovia medium pressure mercury vapor lamp housed in a Pyrex jacketed immersion well. The progress of the reaction was monitored by GC (column: 8 ft × 1/8 in., 10% OV-17) analysis. Photolysis was discontinued after 6 h, and the solvent was removed at atmospheric pressure by distillation. The crude concentrate was analyzed by GC as well as GC–MS (column: 25 mts capillary, methyl silicone). The peaks were characterized by coinjection with the authentic samples and were also confirmed by spectral identification. GC yields of the products are given in Table 2. The other selenides 2–4 were irradiated in a similar manner as described for 1.

PET Reaction of the Neopentyl Phenyl Selenide (8). A mixture of 8 (0.171 g, 3.0 mM) and DCN (0.013 g, 0.3 mM) in 250 mL of methanol was irradiated in a similar manner as described for 1. Irradiation was discontinued (8 h) when 80% consumption of 8 was noticed by GC (column: 8 ft × 1/8 in., 10% OV-17). Usual workup and the analysis of the crude photolysate mixture by GC displayed two peaks besides PhSeSePh. The new peaks were characterized as 9 and 10 by coinjection with the authentic samples. The GC yields of 9, 10, and PhSeSePh were calculated based on the consumption of 8 and are found to be 35%, 15%, and 50%, respectively.

General Method for the PET Deselenylation Reaction of 11–16. A mixture of 11 (0.304 g, 4.0 mM) and DCN (0.0178 g, 0.4 mM) in 250 mL of methanol was irradiated in an identical manner as described for 1. Progress of the reaction was monitored by GC analysis (column: 8 ft × 1/8 in., 10% OV-17). Eighty percent consumption of 11 was noticed after

8 h of irradiation. At this stage irradiation was discontinued due to the precipitation of PhSeSePh, and no further change in disappearance of 11 was observed. Usual workup and purification of crude photolysate by silica gel column chromatography using EtOAc:hexanes (1:19) as eluent gave 0.125 g of 17 in 70% yield. IR (neat): 1580, 1480, 1440, 1200, 1120, 780, 730 cm^{-1}. ^{1}H NMR (CDCl$_3$, 200 MHz): δ 6.85 (d, 1H, J = 8.0 Hz), 6.80 (d, 1H, J = 8.0 Hz), 6.60 (t, 1H, J = 8.0 Hz), 4.95 (m, 1H), 3.55 (m, 2H), 3.45 (s, 3H), 3.20–3.10 (dd, 1H, J = 9.7 and 14.6 Hz), 2.95–2.85 (dd, 1H, J = 9.7 and 14.6 Hz) and 2.25 (s, 3H). ^{13}C (CDCl$_3$, 50.4 MHz): δ 158.07, 129.29, 125.56, 122.32, 120.36, 119.63, 81.15, 74.91, 59.37, 32.57 and 15.29. MS m/z (relative intensity): 178 (M$^+$, 75), 145 (100), 133 (95), 105 (70), 91 (30). Anal. Calcd for C$_{11}$H$_{14}$O$_2$: C, 74.13; H, 7.91. Found: C, 74.02; H, 8.14. DCN was recovered quantitatively (0.0174 g, 98%). 12–16 were also irradiated in the similar manner as described for 11. All the deselenylated products were characterized by IR, ^{1}H NMR, ^{13}C NMR, and mass spectral data.

21. IR (neat): 1460, 1160, 1070 cm^{-1}. ^{1}H NMR (CDCl$_3$, 200 MHz): δ 4.25 (m, 1H), 3.50–3.25 (m, 5H), 3.20 (m, 1H) and 2.20–1.00 (m, 11H). ^{13}C (CDCl$_3$, 50.4 MHz): δ 83.87, 82.56, 77.85, 76.01, 75.86, 59.16, 59.06, 45.75, 44.30, 34.01, 33.48, 31.35, 29.11, 28.96, 25.81, 25.72, and 24.29. MS m/z (relative intensity): 170 (M$^+$, 5), 169 (20), 138 (20), 125 (100), 107 (45), 81 (25). Anal. Calcd for C$_{10}$H$_{18}$O$_2$: C, 70.55; H, 10.65. Found: C, 70.61; H, 10.53.

General Method for the One-Pot Selenylation–Deselenylation PET Reaction. A dilute solution containing a mixture of 5-hexen-1-ol (7, 0.50 g, 10.0 mM), PhSeSePh (0.78 g, 5.0 mM), and DCN (0.089 g, 1.0 mM) in 500 mL of methanol was irradiated for 8 h under the identical conditions as described earlier. GC analysis showed a peak corresponding with the identical retention time of 12, which was finally confirmed by coinjection with the authentic sample of 12. Continued irradiation (30 h, 90% consumption of 7) of the reaction mixture led to the complete disappearance of 12 and the appearance of a new peak corresponding to 18. Usual workup and purification of the crude photolysate by silica gel column chromatography using ether:pentane (1:99) as eluent gave 18 (0.46 g, 70% yield). The spectral values of this product were found to be in good agreement with the authentic sample of 18.

Supplementary Material Available: Experimental procedures and spectral characterization of 1–4, 8, 11–16, 18–20, 22, 24, and 25. Stern–Volmer plots for fluorescence quenching of DCN by 1–4 (Figure 1), correlation plot of log-$[K_{q}]$ *vs* $E_{1/2}^{ox}$ of 1–4 (Figure 2), and double reciprocal plot of $[\phi_{disap}]$ *vs* concentration of 1–4 $[\phi_{disap}^{-1}$ *vs* $[1-4]^{-1}]$ (Figure 3) (8 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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