Photosensitized Electron Transfer Promoted Reductive Activation of Carbon−Selenium Bonds To Generate Carbon-Centered Radicals: Application for Unimolecular Group Transfer Radical Reactions

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The investigation presented in this paper explores the mechanistic aspects and synthetic potentials of photosensitized electron transfer (PET) promoted reductive activation of organoselenium substrates. PET activation of substrates **1**−**5** is achieved through a photosystem comprised of light-absorbing 1,5-dimethoxynaphthalene (DMN) as electron donor and ascorbic acid as co-oxidant. The fluorescence quenching of ^{1}DMN* by organoselenium compounds **1**−**5**, correlation of fluorescence quenching rate constant with the reduction potentials of **1**−**5**, and the dependence of photodissociation quantum yields of **1**−**5** on their concentration suggests the occurrence of electron-transfer (ET) processes between ^{1}DMN* and **1**−**5**. Steady state photolysis of organoselenium substrates ($R_2CHSePh$) in the presence of ^{1}DMN* and ascorbic acid leads to the cleavage of the −C−Se− bond to produce a carbon-centered radical and $PhSe^-$ species *via* the intermediacy of $R_2CH-SePh]^{-\bullet}$. The mechanistic interpretation for the reductive activation of −C−Se− bonds and the synthetic utility of observed cleavage pattern is extended for the unimolecular group transfer radical sequences.

Introduction

Addition or removal of electrons activates molecules for mesolytic cleavage[1] (fragmentation of radical ions), providing a useful method of breaking bonds that are otherwise strong in neutral substrates. In this context, photopromoted exchange of electrons between two interacting substrates has acquired prominence over the past decade,[2] as photoexcitation renders well-defined redox potential differences between interacting substrates—a requisite for electron to exchange. The uniqueness 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 is the case during the normal photochemical reactions.[3,4] In fact, the facile cleavage of these radical ions into radicals and ions[5,6] has allowed this concept to serve as the basis for the development of many useful organic synthetic reactions.[7,8] Inspite of the remarkable progress made in the area of PET initiated reactions, the focus has remained mainly on the chemistry originating from the mesolysis of radical cations,[5,6] despite the great synthetic potentials of photosensitized one electron reductions in organic synthesis. Fragmentation of radical cations is generally associated with the loss of electrofugal group (H^+ [2c,6a,9]) or metal cations (MR_3^+,[6a,10] M = Pb, Sn, Si, Ge from group 4A organometallics) leads to the generation of carbon-centered radicals. However, a contrasting observation was made from our group while studying the fragmentation pattern of PET-generated $R_3CSePh]^{+\bullet}$ where the radicals are associated with the selenium group and the cationic charge is retained with the carbon atom.[11] This unusual cleavage pattern encouraged us to explore the reactivity profiles of unexplored PET-generated radical anions from organoselenium compounds. Apart from a mechanistic interest, this study is undertaken with a view to develop a novel unimolecular phenylselenyl group transfer radical reaction, a superior concept[12] in radical chemistry, from the organoselenium substrates of **type-1 (7)** provided the cleavage of $R_3CSe-]^{-\bullet}$ occurs as depicted in Scheme 1.

The full details of the study[13] presented in this paper unravel the generation of $R_3CSe-]^{-\bullet}$ by one-electron transfer through a photosystem comprised of 1,5-dimethoxynaphthalene (DMN) as light-harvesting electron donor and ascorbic acid as co-oxidant. The synthetic potentials of the cleavage of $R_3CSe-]^{-\bullet}$ from substrates

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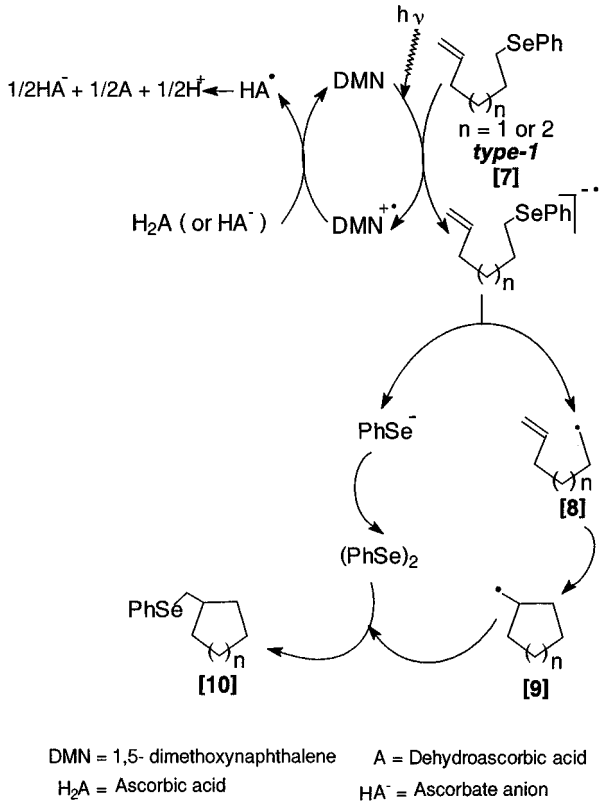
Scheme 1



of **type-1 (7)** are explored, and its utility for the unimolecular group transfer (UMGT) radical reactions is demonstrated. Steady state analysis of the fluorescence quenching of DMN and the dependence of R_3CSePh bond cleavage quantum yield on quencher concentration (DMN) also form a part of the complete mechanistic study of the PET reductive phenomenon from organoselenium substrates.

Results and Discussion

To generate radical anions from −C−Se− bond compounds **[1**−**5]**, a photosystem comprised of DMN as light-harvesting electron donor and ascorbic acid as sacrificial electron donor is utilized as shown in Scheme 1. The thermodynamic feasibility of electron transfer (ET) from ^{1}DMN* to **1**−**5** is established by estimating the free energy change (ΔG_{et}) associated with ET processes by the Weller equation[14] (eq 1), where $E_{1/2}^{ox}$[D] is the oxidation potential of DMN, $E_{1/2}^{red}$[A] is the reduction potential of the acceptors **1**−**5** and $E_{0,0}$ is the excitation energy of DMN.

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

Substituting eq 1 with the appropriate values of the reduction potentials of **1**−**5** (−1.00 to −0.29 eV/SCE), obtained by cyclic voltammetry (for details see Experimental Section), the oxidation potential of DMN* (1.28 eV),[15] and the excitation energy (87.8 kcal M^{-1})[15] gave exergonic (−35.22 to −51.60 kcal M^{-1}) values for all the compounds (Table 1).

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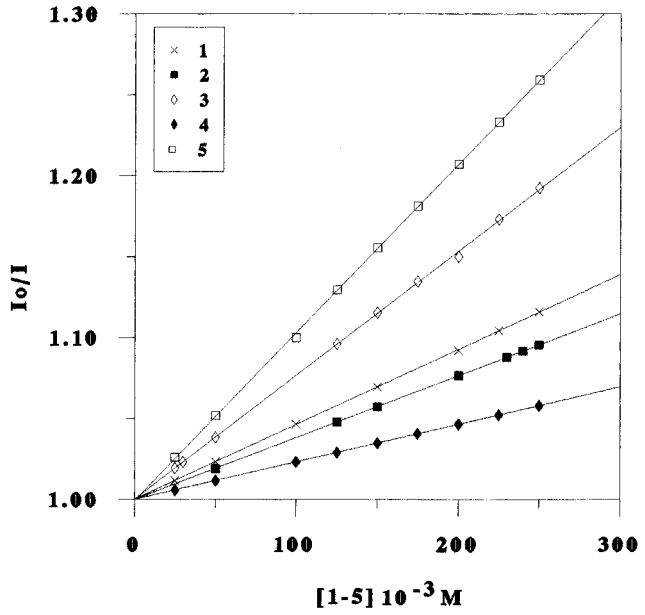

Figure 1. Stern−Volmer plots for fluorescence quenching of DMN by selenides **1**−**5**.

Further evidence of ET processes for these systems could be obtained by studying the fluorescence quenching of DMN (λ_{exi} = 300 nm, λ_{emi} = 344 nm) by **1**−**5** which obeys the Stern−Volmer relation **(**Figure 1). From the slopes ($K_{qf}\tau$) of the straight lines **(**Figure 1), and singlet lifetime (τ = 12.6 ns)[15] of DMN, the quenching rate constants (K_{qf}) are calculated (correlation coefficient > 0.99, S.D. = 0.005) and are found to be near diffusion[2b] ($K_{diff} = 2.30 \times 10^{10}$ M^{-1} s^{-1}, Table 1). Excitation and absorption spectra of DMN remains unaffected in the presence of the maximum concentration of **1**−**5**. No exciplex emission is noticed in either polar or nonpolar solvents. Quenching due to heavy atom induced intersystem crossing could also be suggested to be minimal, based on logic similar to that provided by Eaton et al.[10c] It is, therefore, reasonable to assume that fluorescence quenching in these cases takes place *via* a charge transfer (CT) stabilized exciplex. Convincing proof of ET in these systems may further be obtained through a linear correlation plot (Figure 2) of log[K_{qf}] *vs* $E_{1/2}^{red}$ of **1**−**5**. Similarly, ET feasibility from ascorbic acid to $DMN^{+\bullet}$ is evaluated by estimating ΔG_{et} (−4.51 kcal M^{-1}) employing the equation $E_{1/2}^{ox} - E_{1/2}^{red}$. The $E_{1/2}^{ox}$ value (1.084 eV/SCE) for ascorbic acid is estimated by cyclic voltammetry.[16] The electron-donating ability of ascorbate ion and its transformation to the dehydroascorbic acid and proton is precedented from the literature report.[17]

Since PET reaction from a donor−acceptor pair in solvents of high dielectric constant results in the formation of free radical ions (FRIP) *via a* solvent-separated ion pair (SSIP), in competition with back electron transfer,[18] the ET from ^{1}DMN* to **1**−**5** is envisioned to lead the chemistry predominantly from the free radical anions of the organoselenium substrates **(1**−**5)** where the chances of intermolecular coupling between the donor−acceptor

(16) Since the reduction potential of ascorbic acid is irreversible, the ΔG_{et} value obtained is only approximate; however it agrees generally quite well with the experimental value.
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Table 1. Physical Constants Evaluated for PET from Organoselenium Substrates (1−5)

selenides	K_{qf}[a,b] ($\times 10^{10}$ MS^{-1})	K_{qr}[a,c] ($\times 10^{10}$ MS^{-1})	$E_{1/2}^{red}$[d] (eV)	ΔG_{ee}[e] (kcal M^{-1})	$\phi_{disappearance}$[a,f]	ϕ_{lim}[a,f,g]
1	0.368 ± 0.001	0.361 ± 0.003	−0.70	−42.14	0.026 ± 0.004	0.083 ± 0.002
2	0.303 ± 0.005	0.288 ± 0.002	−0.80	−39.83	0.023 ± 0.006	0.068 ± 0.005
3	0.611 ± 0.002	0.623 ± 0.005	−0.60	−44.45	0.080 ± 0.003	0.128 ± 0.007
4	0.184 ± 0.003	0.211 ± 0.004	−1.00	−35.22	0.013 ± 0.007	0.049 ± 0.003
5	0.822 ± 0.005	0.782 ± 0.007	−0.29	−51.60	0.095 ± 0.004	0.130 ± 0.005

[a] Errors are standard deviations from the average. [b] From the fluorescence quenching Stern−Volmer plot. [c] From the double-reciprocal plot; $(\phi_{disappearance})^{-1}$ *vs* $[\mathbf{1}-\mathbf{5}]^{-1}$. [d] Referenced to saturated calomel electrode (SCE) using tetraethylammonium perchlorate as supporting electrolyte in dry acetonitrile. [e] Oxidation half-wave potential for DMN = 1.28 eV and $E_{0,0}$ = 3.807 eV. [f] Light intensity was evaluated by uranyl oxalate actinometry; for details see Experimental Section. [g] At infinite donor concentration; measured from the plot of $(\phi_{disappearance})^{-1}$ *vs* $[\mathbf{1}-\mathbf{5}]^{-1}$.

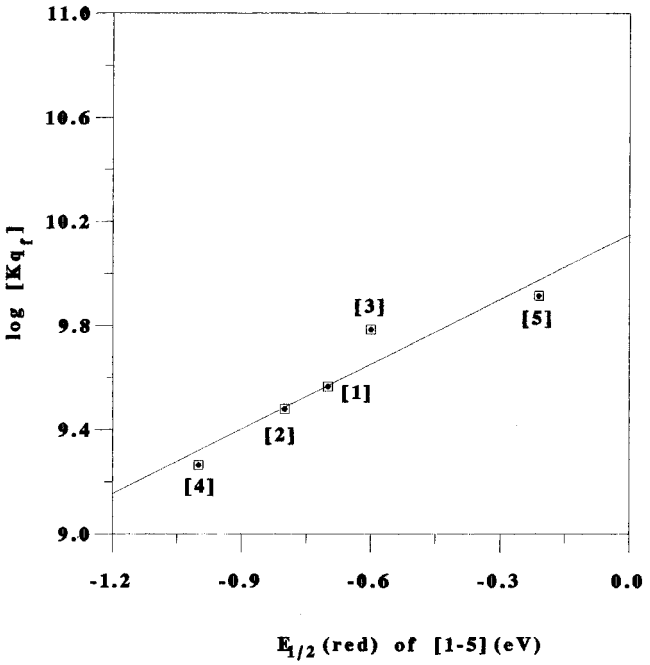
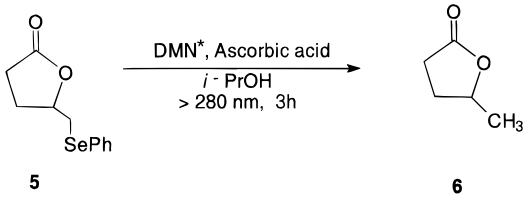


Figure 2. Correlation plot of $\log[K_{qf}]$ *vs* $E_{1/2}^{red}$ of **1**−**5**.

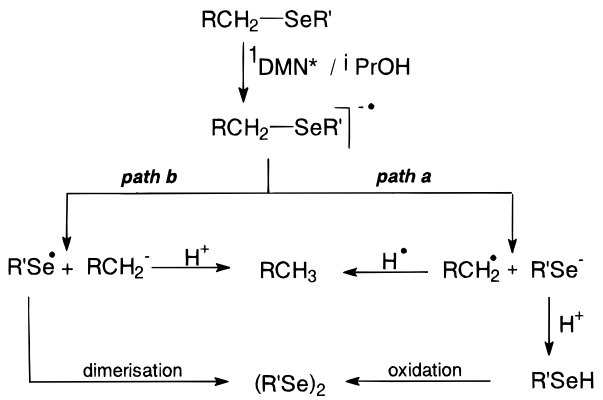
Scheme 2



5 **6**

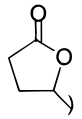
pair would be minimal. To probe this aspect, organoselenium substrate **5** (0.98 mmol) is irradiated in a 2-propanol solution containing DMN (0.25 mmol) and ascorbic acid (0.25 mmol) for 3 h, without removing dissolved oxygen from the solution (Scheme 2). Care has been taken that all the light under this arrangement is absorbed by DMN only. Analysis of the photolysate indicated the formation of deselenylated product **6** (characterized by ^{1}H NMR, ^{13}C NMR, and MS spectral analysis) in 83% yield along with PhSeSePh. DMN is found almost unchanged (99%) at the end of the reaction. A control experiment in which **5** is photolyzed under identical conditions as mentioned above but without DMN failed to show any product, suggesting the sensitized role of DMN for this transformation. The formation of deselenylated product **6** could be explained by the cleavage of −CSe−┤•⁻ following either path a or path b (Scheme 3). However, the PET reaction of **5** in the deuterated 2-propanol (*i*-PrOD) failed to indicate any deuterium incorporation in the product (monitored by ^{1}H

Scheme 3



1. R = CH_3, R' = Ph **2.** R = C_7H_{15}, R' = Ph

3. R = Ph, R' = CH_2Ph **4.** R = C_3H_7, R' = C_4H_9

5. R =  , R' = CH_2SePh

NMR and MS). Therefore, it is reasonable to consider the cleavage of **5** by following path a. The other fragment $PhSe^-$ either can dimerize directly in the presence of oxygen to produce PhSeSePh or it may pick up a proton to form phenylselenol and then dimerize. The quantum yields for the disappearance of **1**−**5** are given in Table 1. To correlate a common reactive species during the photoreaction of **1**−**5** and the mechanism of DMN fluorescence quenching by these substrates, an exciplex with partial CT character is proposed to be formed between ^{1}DMN* and **1**−**5**. A quantitative description to this aspect is derived by correlating the fluorescence quenching constants (K_{qf}) with $\phi_{disappearence}$ of **1**−**5**. A double-reciprocal plot of $\phi_{disappearence}$ *vs* concentration of **1**−**5** ($[\phi_{disappearence}]^{-1}$ *vs* $[\mathbf{1}-\mathbf{5}]^{-1}$) resulted in a straight line (Figure 3). The ratio of the intercept/slope ($K_{qr}\tau$) corresponded almost to the identical values (within the acceptable limits of experimental error) of $K_{qf}\tau$ (Table 1) as obtained from the Stern−Volmer fluorescence quenching analysis. The inverse of the intercept gave a limiting quantum yield (ϕ_{lim}, Table 1) for the disappearance of **1**−**5**.

The efficient PET cleavage of **5** to generate a carbon-centered radical led us to envisage the utilization of −C−Se− bonds in general as carbon radical equivalents, and hence, we decided to explore the synthetic potentials of such fragmentations for UMGT radical reactions, since

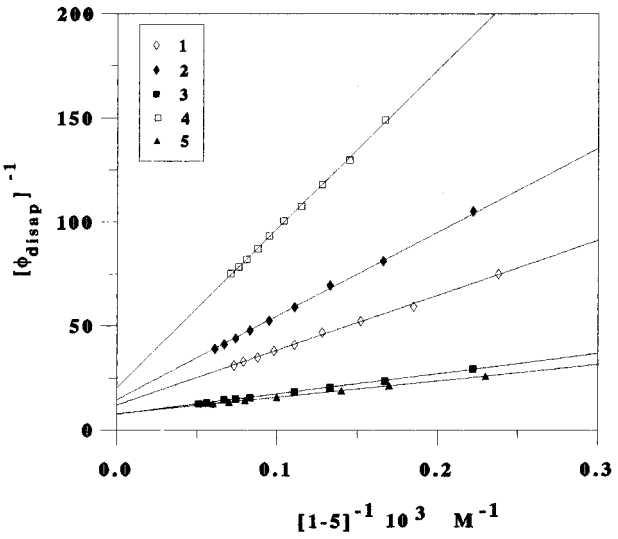
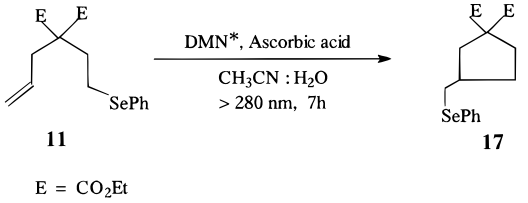


Figure 3. Double-reciprocal plot of $\{(\phi_{disap})^{-1}$ *vs* $[\mathbf{1}-\mathbf{5}]^{-1}\}$.

PhSeSePh, a good radical trapping agent,[19] is produced in the process. Most of the existing methodologies for radical reactions are based on tin hydride,[20] despite its inherent limitations such as toxicity and difficulty in removing tin byproducts. The serious disadvantage[21] of the tin hydride system lies in the loss of functionality due to the termination of radical sequence by hydrogen abstraction and reduction of the starting radical under normal experimental conditions. Although some partial solutions to these problems have been addressed by introducing rather expensive reagents,[22] the atom transfer approach,[23] or utilizing modified tin-based reagents,[21] a practical solution to this has remained elusive. In this context, it was envisaged that PET reaction from organoselenium compounds containing a proximate Π-bond in non-hydrogen donating solvents would lead to the formation of cyclized products through the sequences as outlined in Scheme 1. These expectations were born out in practice by irradiating a mixture containing **11** (1.3 mmol), DMN (0.50 mmol), and ascorbic acid (0.50 mmol) in CH_3CN-H_2O (4:1) without removing dissolved oxygen from the solution. Removal of the solvent followed by usual workup and purification furnished **17** as a major product in 88% yield **(**Scheme 4**)**. To test the generality of the UMGT radical reaction concept, compounds **12**−**16** were irradiated, and results are listed in Table 2. Substrates **11**−**12** are prepared by nucleophilic displacement of *in situ* generated phenylselenyl anion on the corresponding halide,[24a] while compounds **13**−**16** are made by following the reported procedure.[24b] All the five-membered cyclization yields are above 70%, and the stereochemistries of the products **(19**−**22**) are in accordance with the Beckwith rules.[25] Six-membered cyclization yields are very poor and in case of **12b** the photolysis resulted in an uncharacterizable mixture of products.

Scheme 4



11 **17**

E = CO_2Et

From the reaction **(**Scheme 4**)** it is obvious that there will not be quantitative transformation of **11** to **17** due to the time lag for the accumulation of PhSeSePh, required for the termination of radical sequences. Therefore, to quantify this aspect, quantum efficiencies for the $\phi_{disappearance}$ of **11** and $\phi_{appearance}$ of **17** are compared and a difference of 11.45% is observed indicating that only 11.45% of **11** is unaccounted for in this reaction. Complete conversion of **11** to **17** can be achieved by performing the PET reaction containing a trace amount of PhSeSePh in the initial reaction mixture.

In conclusion, we have demonstrated a mechanistically interesting photoinduced ET activation of −C−Se− bonds to generate carbon-centered radicals and its synthetic utility toward UMGT radical reactions.

Experimental Section

General. DMN[15] and PhSeSePh[26] were synthesized and purified by following the literature procedures. **1**−**2**,[24a] **3**,[27] **4**,[28] and **5**[29] were prepared by following reported procedures. Methanol and acetonitrile that are used in HPLC analysis and fluorescence studies, respectively, were of spectroquality (E. Merck, India) grade. Silica gel for column chromatography (finer than 200 mesh) was obtained from Acme, India.

All nuclear magnetic resonance spectra were recorded on either Bruker AC 200 FT NMR or Brucker MSL 300 NMR spectrometers using $CDCl_3$ as solvent. All chemical shifts are reported in parts per million downfield 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 a Finnigan MAT-1020B instrument.

Fluorescence spectra were recorded on a Spex-Fluorolog 212 spectrofluorimeter. The excitation and emission slit widths were maintained at 0.5 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 Perkin-Elmer (Model 250 binary LC pump along with LC 135C diode array detector) liquid chromotograph using reverse phase C_{18} (Bondapack 0.5 μm) column, eluting with a $CH_3CN:H_2O$ (75:25) solvent mixture degassed by the freeze−thaw cycle procedure.

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 consisted of a Metro E410 hanging mercury drop electrode

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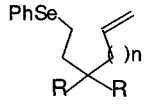
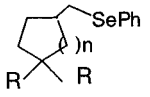
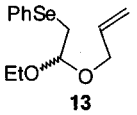
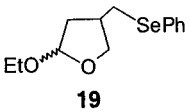
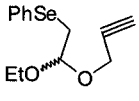
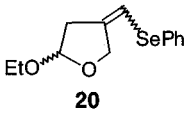
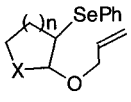
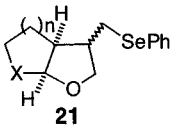
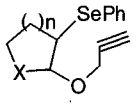
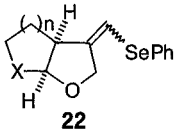
Table 2. Unimolecular Group Transfer Radical Reactions

Entry	Substrate[a]	Product[b,c]	*cis* / *trans* (or)E / Z[d]	Yield (%)[e]
1.	 **12**	 **18**		
	a) n = 1 ; R = H		-	80
	b) n = 2 ; R = H		-	-
	c) n = 2 ; R = $CO_2C_2H_5$		-	10
2.	 **13**	 **19**	16 / 84	84
3.	 **14**	 **20**	32 / 68	78
4.	 **15**	 **21**		
	a) n = 1 ; X = CH_2		64 / 36	75
	b) n = 2 ; X = O		82 / 18	82
5.	 **16**	 **22**		
	a) n = 1 ; X = CH_2		66 / 34	71
	b) n = 2 ; X = O		88 / 12	78

a) See supplementary material for the preparation and characterization of 12 - 16. ; *b*) characterized by ^{1}H NMR, ^{13}C NMR and Mass spectra ; *c*) cis / trans and E / Z ratios are confirmed by using HPLC ; isomers were not seperable by column chromotography ; *d*) In case of 21b and 22b only major isomer was isolated. Minor isomer was not obtained in enough quantity for spectral characterization ; *e*) Isolated yields, but not optimized.

(HMDE) and Pt wire (auxiliary electrode). The supporting electrolyte was tetraethylammonium perchlorate, and potentials are referred to SCE and are uncorrected for liquid junction potentials.

Fluorescence Quenching. Quenching of DMN fluorescence was carried out by using **1**−**5** as quenchers. For the determination of Stern−Volmer constants (K_{qf}), the intensity (I_0) of steady state fluorescence at the maximum emission (λ_{emi}) 344 nm was measured from DMN solution (3×10^{-3} M) in CH_3CN at 25 °C, keeping the excitation wavelength (λ_{exi}) at 300 nm. Subsequently, the fluoresence quenching intensity (I) was measured as a function of concentration [Q] of **1**−**5** in the range of 3×10^{-3} to 250×10^{-3} M. Linear plots were obtained on the basis of the equation $I_0/I = 1 + K_{qf}\tau[Q]$, where I_0 denotes the fluoresence intensity in the absence of quencher. No curvature was noticed in any system, and intercepts were 1.00 ± 0.007 in all cases. Slopes were determined by 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**−**5** into Pyrex tubes, and the samples were irradiated in a quantum yield reactor (Model QYR-20) using a 200-W mercury lamp. Irradiations were carried out for a short interval of time to bring about only 8−10% of the conversion. A uranyl oxalate actinometer was used to monitor the intensity of light.[30] Quantitative loss of the selenides **1**−**5** was estimated by HPLC [column C_{18}, eluent CH_3CN:H_2O (3:1)] while loss of **4** was estimated by 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**−**5**) was obtained from the inverse plot of the variable donor concentrations (6×10^{-3} to 27×10^{-3} M) *vs* quantum yields i.e., $[\mathbf{1}-\mathbf{5}]^{-1}$ *vs* $\Phi_{disappearance}^{-1}$, by keeping the DMN concentration fixed at 3×10^{-3} M.

Photoirradiation of 5. A mixture of **5** (0.25 g, 0.98 mmol), DMN (0.05 g, 0.27 mmol), and ascorbic acid (0.05 g, 0.27 mmol) in 250 mL of 2-propanol was irradiated at room temperature, without removing dissolved oxygen, with a 450-W Hanovia medium pressure mercury vapor lamp housed in a Pyrex-jacketed immersion well. The progress of the reaction was monitored by GC analysis. Photolysis was discontinued after 3 h, and solvent was removed at reduced pressure. The crude concentrate purified by column chromatography gave 0.27 mg

(30) Murov, S. L. *Hand Book of Photochemistry*; Marcel Dekker: New York, 1973; p 124.

(78% yield) of deselenylated product **(6)**. This product was identified by comparing its spectral data with that reported in the literature.[29]

General Method for PET UMGT Radical Chain Reaction. A mixture of **11** (0.50 g, 1.30 mmol), DMN (0.10 g, 0.50 mmol), and ascorbic acid (0.09 g, 0.50 mmol) in 500 mL of CH_3CN was irradiated at room temperature with a 450-W Hanoiva medium pressure mercury vapor lamp housed in a Pyrex-jacketed immersion well, without removing dissolved oxygen. The progress of the reaction was monitored by HPLC analysis. Photolysis was discontinued after 7 h, and the solvent was removed at reduced pressure. The crude concentrate purified by column chromatography gave cyclized product **17** (0.39 g) in 79% yield. The product **17** was characterized by ^{1}H NMR, ^{13}C NMR, and mass spectral analysis.

17: IR (neat) 3070, 2860, 1710 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.25 (t, 6H, J = 9.75 Hz), 1.45 (m, 1H), 1.90 (m, 2H), 2.25 (m, 3H), 2.55 (m, 1H), 2.95 (d, 2H, J = 4.75 Hz), 4.20 (q, 4H, J = 9.75 Hz), 7.25 (m, 3H), 7.55 (m, 2H); ^{13}C NMR (50.32 MHz, $CDCl_3$) δ 172.57, 132.96, 129.27, 127.06, 61.61, 60.41, 40.94, 40.24, 34.06, 33.48, 32.64, 14.27; MS *m*/*e* (relative intensity) 384 (M$^+$, 18), 339 (7), 227 (52), 119 (27), 153 (100), 79 (28). Anal. Calcd for $C_{18}H_{24}O_4Se$: C, 56.39; H, 6.31. Found: C, 56.34; H, 6.29.

An identical irradiation procedure was adopted for the UMGT cyclization reactions of **12**−**16**, and spectral characteristics of **18**−**22** are given as follows.

18a: IR (neat) 3070 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.55 (m, 6H), 1.7 (m, 3H), 2.85 (d, 2H, J = 4.5 Hz), 7.25 (m, 3H), 7.50 (m, 2H); ^{13}C NMR (50.32 MHz, $CDCl_3$) δ 13.15, 20.92, 28.75, 36.98, 120.15, 127.23, 129.15, 130.52, 132.84, 134.46; MS *m*/*e* (relative intensity) 240 (M$^+$, 51), 171 (100), 157 (47), 83 (55).

19: IR (neat) 3070, 1200, 1125 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.20 (t, 3H, J = 9.7 Hz), 1.75 (m, 1H), 2.20−2.50 (m, 2H), 3.00 (m, 2H), 3.45 (m, 1H), 3.75 (m, 2H), 4.05 (t, 1H, J = 9.7 Hz), 5.15 (m, 1H), 7.25 (m, 3H), 7.55 (m, 2H); ^{13}C NMR (50.32 MHz, $CDCl_3$) δ 132.97, 131.60, 130.00, 129.26, 129.18, 127.79, 127.09, 104.20, 104.01, 72.04, 62.99, 62.78, 39.86, 39.64, 38.67, 37.91, 32.33, 31.54, 15.42, 15.33; MS *m*/*e* (relative intensity) 286 (M$^+$, 286), 240 (15), 157 (23), 91 (42), 83 (100). Anal. Calcd for $C_{13}H_{18}O_2Se$: C, 54.74; H, 6.36. Found: C, 54.53; H, 6.38.

20: IR (neat) 3085, 1620, 1200, 1129 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.25 (t, 3H, J = 8.1 Hz), 2.75 (m, 2H), 3.50 (m, 1H), 3.80 (m, 1H), 4.50 (m, 2H), 5.35 (m, 1H), 6.40 (m,1H), 7.25 (m, 3H), 7.55 (m, 2H); ^{13}C NMR (50.32 MHz, $CDCl_3$) δ 145.24, 143.83, 131.55, 131.29, 131.16, 129.24, 127.73, 126.89, 126.80, 108.44, 107.59, 103.51, 69.66, 69.44, 62.79, 62.65, 40.73, 39.60, 15.26; MS *m*/*e* (relative intensity) 284 (M$^+$, 1), 157 (15), 129 (100), 115 (23), 91 (16). Anal. Calcd for $C_{13}H_{16}O_2Se$: C, 55.13; H, 5.69. Found: C, 54.89; H, 5.71.

21a: IR (neat) 3080, 1615, 1125 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.65−1.85 (m, 4H), 2.60 (m, 1H), 3.00 (m, 2H), 3.45 (m, 1H), 3.95 (m, 1H), 4.55 (m, 1H), 7.30 (m, 3H), 7.55 (m, 2H); ^{13}C NMR (75.47 MHz, $CDCl_3$) δ 132.88, 132.54, 130.25, 130.03, 129.02, 126.98, 126.84, 86.18, 85.15, 73.31, 72.17, 50.07, 47.97, 47.04, 43.37, 34.46, 34.01, 32.32, 30.73, 26.34, 25.93, 25.21, 24.05; MS *m*/*e* (relative intensity) 282 (M$^+$, 10), 157 (15), 124 (17), 107 (20), 95 (75), 67 (100). Anal. Calcd for $C_{14}H_{18}OSe$: C, 59.79; H, 6.45. Found: C, 59.55; H, 6.43.

21b: IR (neat) 3085, 1210, 1122 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.60 (m, 4H), 2.15 (m, 1H), 2.65 (m, 1H), 2.95 (m, 2H), 3.70 (m, 3H), 4.05 (t, 1H, J = 7.15 Hz), 5.25 (d, 1H, J = 4.3 Hz), 7.30 (m, 3H), 7.55 (m, 2H); ^{13}C NMR (75.47 MHz, $CDCl_3$) δ 132.90, 129.33, 128.95, 127.04, 101.62, 69.92, 60.90, 40.93, 37.21, 25.60, 22.80, 19.05; MS *m*/*e* (relative intensity) 298 (M$^+$, 6), 197 (20), 157 (12), 141 (51), 116 (42), 95 (33), 77 (55), 69 (88), 55 (100). Anal. Calcd for $C_{14}H_{18}O_2Se$: C, 56.57; H, 6.10. Found: C, 56.45; H, 6.11.

22a: IR (neat) 3085, 1645, 1210 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.60−1.75 (m, 6H), 2.75 (m, 1H), 3.60 (m, 2H), 4.05 (t, 1H, J = 4.3 Hz), 6.65 (m, 1H), 7.30 (m, 3H), 7.55 (m, 2H); ^{13}C NMR (75.47 MHz, $CDCl_3$) δ 145.75, 146.01, 133.12, 133.99, 129.75, 129.30, 129.04, 117.75, 117.23, 83.02, 82.95, 74.45, 73.82, 46.15, 45.99, 37.91, 37.72, 33.35, 32.47, 26.75, 25.21; MS *m*/*e* (relative intensity) 280 (M$^+$, 3), 157 (16), 123 (100), 109 (20), 91 (15). Anal. Calcd for $C_{14}H_{16}OSe$: C, 60.22; H, 5.78. Found: C, 59.99; H, 5.76.

22b: IR (neat) 3085, 1625, 1200, 1129 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.65 (m, 5H), 2.75 (m, 2H), 3.50 (m, 1H), 3.80 (m, 1H), 4.50 (m, 2H), 5.35 (m, 1H), 6.40 (s, 1H), 7.25 (m, 3H), 7.55 (m, 2H); ^{13}C NMR (50.32 MHz, $CDCl_3$) δ 144.97, 132.85, 129.03, 128.99, 127.33, 101.55, 69.95, 61.05, 41.21, 25.06, 23.12; MS *m*/*e* (relative intensity) 296 (M$^+$, 7), 157 (18), 139 (100), 125 (22), 91 (28). Anal. Calcd for $C_{14}H_{16}O_2Se$: C, 56.96; H, 5.46. Found: C, 56.79; H, 5.44.

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