

Photoinduced Single Electron Transfer Initiated Heterolytic Carbon-Selenium Bond Dissociation. Sequential One-Pot Selenenylation and Deselenenylation Reaction

Ganesh Pandey,* B. B. V. Soma Sekhar, and U. T. Bhalerao

Organic Division
Indian Institute of Chemical Technology[†]
Hyderabad 500 007, India

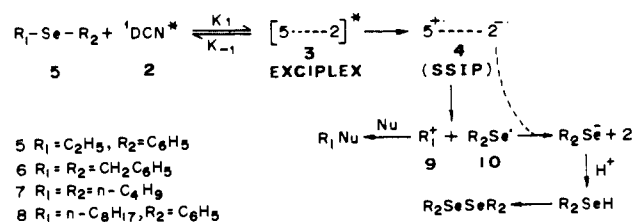
Received July 18, 1989

Recently we have reported in situ generation of electrophilic selenium (PhSe^+) species via diphenyl diselenide radical cation ($\text{PhSeSePh}^{+\bullet}$) formed by single electron transfer (SET) from PhSeSePh (**1**) to the excited singlet of 1,4-dicyanonaphthalene (DCN, **2**).¹ We report herein electron transfer (ET) from compounds possessing a carbon-selenium bond to $^1\text{DCN}^*$ leading to heterolytic C-Se bond dissociation via a radical cation intermediate with concurrent demonstration of a new, very mild, synthetically promising way of effecting deselenenylation reactions.

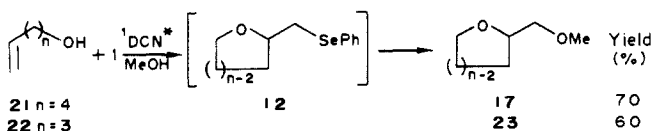
Organoselenium compounds **5-8** (Scheme I) efficiently quench the fluorescence of **2** with a diffusion-controlled² rate constant, (K_{qET}). Emission and absorption spectroscopic properties of mixtures of **5-8** and **2** fail to reveal ground or excited state complex formation in polar and nonpolar solvents. A SET mechanism for the fluorescence quenching of **2** by **5-8** is supported by the endoergic value for the free energy change (ΔG_{ET}) estimated by the Weller equation³ and the correlation plot of $\log K_{\text{qET}}$ vs $(E_{1/2}(\text{ox}))^4$ of **5-8**, which showed a linear relationship⁵ (Table I). This suggested the possibility of performing photosensitized SET initiated reaction from compounds **5-8**. To test this concept, we irradiated⁶ (>280 nm) a mixture of **5-8** (3 mM) with **2** (0.3 mM) in methanol, for which the details are given in Table I. Bibenzyl formation from compound **6** seems to occur by deselenenylation of $\text{PhCH}_2\text{Se}^{\bullet}$ ($\text{PhCH}_2\text{Se}^{\bullet} \rightarrow \text{PhCH}_2^{\bullet} + \text{Se}$), which is evident from the observation of only a trace amount of bibenzyl (3-6%) compared to other products.⁷

The above results can be rationalized with reference to Scheme I, which considers the intermediacy of an exciplex with partial charge-transfer character. A double reciprocal plot of quantum yield (ϕ_{dissap}) vs **5-8** concentration (ϕ^{-1} vs $[\text{Q}]^{-1}$) resulted a straight line with an identical $K_{\text{qET}}\tau$ (intercept/slope) as obtained from fluorescence measurements (Table I), which supports the above argument. Electron transfer between **5-8** and **2** results in generation of the solvent-separated ion pair (SSIP). The corresponding radical cation undergoes C-Se bond cleavage (58 kcal/mol),⁸ the carbonium ion escaping and the radical reacting in the cage. In the polar media R_1^+ is more stabilized than the radical $\text{R}_2\text{Se}^{\bullet}$ so that the former diffuses and the latter reacts with

Scheme I



Scheme II

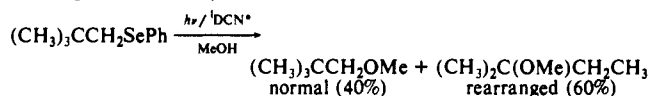


DCN^{••} preferentially to the reverse ET processes. This is supported by trapping of cation by nucleophile and quantitative recovery of DCN. Similar cleavage reactions are known in the case of alkylbenzene and bibenzyl radical cations.⁹ Product analysis (Table I) indicates that a carbocation was always retained on the alkyl group from compounds **5-8**. Free carbocation formation in these reactions is supported by observation of carbocationic rearranged product from the irradiation¹⁰ of neopentyl phenyl selenide, but the ratio of rearranged ether (60%) to normal ether (40%) was different from that in the normal neopentyl carbocation rearrangement, which gives mainly rearranged product.¹¹ This indicates that a carbocation in a solvent cage is readily trapped by a nucleophile before rearrangement can occur, which is evident from our observation that no rearranged carbocationic products were detected from **7** and **8**. Alternatively, the reaction of nucleophile with radical cation prior to cleavage could be ruled out since the latter is a "forbidden" process as the bond formation between the two reactants requires high activation energy.^{12,13}

Since deselenenylation is an important step after synthetic manipulations using organoselenium reagents, a milder and effective approach for this purpose is always desirable. However, existing methodologies for deselenenylation by oxidative¹⁴ or reductive¹⁵ processes suffer from various disadvantages. Our present observation of facile C-Se bond cleavage encouraged us to extend this reaction as a novel procedure for deselenenylation reactions. Irradiation of a mixture of **11-15** (4 mM) and **2** (0.4 mM) in

(9) (a) Albini, A.; Fasani, E.; Mella, M. *J. Am. Chem. Soc.* **1986**, *108*, 4119. (b) Reichel, L. W.; Griffin, G. W.; Muller, A. J.; Das, P. K.; Ege, S. N. *Can. J. Chem.* **1984**, *62*, 424. (c) Davis, H. F.; Das, P. K.; Reichel, L. W.; Griffin, G. W. *J. Am. Chem. Soc.* **1984**, *106*, 6968. (d) Hutchins, R. O.; Learn, K. *J. Org. Chem.* **1982**, *47*, 4380. (e) Nicolaou, K. C.; Claremon, D. A.; Barnette, W. E.; Seitz, S. P. *J. Am. Chem. Soc.* **1979**, *101*, 3704.

(10) Photolysis of neopentyl phenyl selenide gave both normal (40%) and rearranged (60%) methyl ethers:



(11) March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley Eastern Ltd.: New Delhi, 1986; p 944.

(12) (a) Pross, A.; Shaik, S. S. *Acc. Chem. Res.* **1983**, *16*, 363. (b) Ebersson, L.; Blum, Z.; Helgee, B.; Nyberg, B. *Tetrahedron* **1978**, *34*, 731.

(13) Partial out of cage reaction from a free radical ion pair (FRIP) cannot be ruled out completely. Further study concerning this matter is in progress and will be published later.

(14) Jones, D. N.; Mundy, D.; Whitehouse, R. D. *J. Chem. Soc. D* **1970**, 86. (b) Sharpless, K. B.; Lauer, R. F. *J. Am. Chem. Soc.* **1973**, *95*, 2697. (c) Sharpless, K. B.; Lauer, R. F.; Teranishi, A. Y. *J. Am. Chem. Soc.* **1973**, *95*, 6137. (d) Hori, T.; Sharpless, K. B. *J. Org. Chem.* **1978**, *43*, 1689. (e) Reich, H. J.; Reich, I. L.; Renga, J. M. *J. Am. Chem. Soc.* **1973**, *95*, 5813. (f) Reich, H. J.; Wollowitz, S.; Trend, J. E.; Chow, F.; Wendelsorn, D. F. *J. Org. Chem.* **1978**, *43*, 1697.

(15) (a) Nicolaou, K. C.; Magolda, R. L.; Sipio, W. J.; Barnette, W. E.; Lysenko, Z.; Joulie, M. M. *J. Am. Chem. Soc.* **1980**, *102*, 3784. (b) Ley, S. V.; Murray, P. J. *J. Chem. Soc., Chem. Commun.* **1982**, 1252. (c) Danielli, B.; Lesma, G.; Palmisano, G.; Tolluri, S. J. *J. Chem. Soc., Perkin Trans. I* **1984**, 1237. (d) Back, T. G.; Birss, V. I.; Edwards, M.; Krishna, M. V. *J. Org. Chem.* **1988**, *53*, 3815.

[†] IJCT Communication No. 2425.

(1) Pandey, G.; Rao, V. J.; Bhalerao, U. T. *J. Chem. Soc., Chem. Commun.* **1989**, 416.

(2) The singlet lifetime of DCN was taken as 10.1 ns from the following: Arnold, D. R.; Wong, P. C.; Maroulis, A. J.; Cameron, T. S. *Pure Appl. Chem.* **1980**, *52*, 2609.

(3) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.

(4) The cyclic voltammetry experiment was carried out with a three-electrode assembly with 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 electrolyte was tetraethylammonium perchlorate, and potentials are referred to SCE and uncorrected for liquid junction potential. Identical conditions are also used by Atsutaka et al. for determining the electrode potential of diselenides: Atsutaka, K.; Harada, J.; Izumi, J.; Tachihara, H.; Sasaki, K. *Electrochim. Acta* **1983**, *28*, 1361.

(5) Photophysical correlation constants (Table I) do not indicate heavy atom induced intersystem crossing; cf.: Eaton, D. F. *J. Am. Chem. Soc.* **1983**, *103*, 7235.

(6) Irradiation was conducted in a Pyrex vessel by using a Hanovia 450-W lamp.

(7) Similar cleavage of alkylselenium radical from compounds **7** and **8** is not observed.

(8) Paulmier, C. *Selenium Reagents and Intermediates in Organic Synthesis*; Pergamon Press: New York, 1986; Vol. 4, p 6.

Table I. Physical Constants Evaluated for Photoinduced Single Electron Transfer from Organoselenium Compounds (5-8)

substrate	product ^{a,b} composition in MeOH (%)	ϕ_{dissap}^c	ϕ_{im}^d	K_{GET}^e ($\times 10^{10} \text{ M}^{-1} \text{ S}^{-1}$)	K_{GET}^f ($\times 10^{10} \text{ M}^{-1} \text{ S}^{-1}$)	$E_{1/2(\text{ox})}^g$ (eV)	ΔG_{ET}^h
5	PhSeSePh ⁱ	0.012	0.05	1.92 ± 0.005	1.59	1.35	-18.90
6	PhCH ₂ OMe (73) PhCH ₂ CH ₂ Ph (5) (PhCH ₂ Se) ₂ (18) Se metal	0.021	0.12	0.54 ± 0.005	0.54	1.60	-13.08
7	<i>n</i> -C ₄ H ₉ OMe (76.4) (<i>n</i> -C ₄ H ₉ Se) ₂ (23.2)	0.015	0.14	0.47 ± 0.004	0.59	1.65	-11.99
8	<i>n</i> -C ₈ H ₁₇ OMe (61.4) PhSeSePh (38.3)	0.020	0.17	0.44 ± 0.004	0.26	1.62	-12.66

^aCharacterized by identical GC (column: OV-17, 10%) retention time compared with authentic sample and GC mass (column: methyl silicone capillary). ^bThe products mentioned are the primary photoproducts, confirmed by irradiating for shorter periods, and the numbers in parentheses are relative GC yields. ^cLight intensity was evaluated by uranyl oxalate actinometry. ^dAt infinite donor concentration measured from a plot of ϕ^{-1} vs $[Q]^{-1}$. ^eFrom fluorescence quenching Stern-Volmer plot. ^fFrom reciprocal plot of ϕ^{-1} vs $[Q]^{-1}$. ^gReferred to saturated calomel electrode (SCE), using tetraethylammonium perchlorate as supporting electrolyte, in dry acetonitrile (CH₃CN). ^h ΔG_{ET} is expressed in kcal/mol; reductive half-wave potential for DCN ($E_{1/2(\text{red})} = -1.28$ eV) and $E_{0,0} = 3.45$ eV values were used and taken as such from Mattes and Farid: Mattes, S. L.; Farid, S. *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker Inc.: New York, 1983; Vol. 6, p 233. ⁱThe cationic part of the cleavage reaction product (C₂H₅OMe) could not be isolated, possibly due to low boiling point.

Table II. Deselenenylation of Organoselenium Substrates

Entry	Substrates	Products ^a	Yield ^b (%)
1			70
2			80
3			78
4			70
5			60 ^c

^aCharacterized by ¹H NMR and mass spectrometry. ^bIsolated yields, but not optimized. ^cStereochemistry not confirmed.

methanol resulted in a high yield of deselenenylated product (16-20) with no side products (Table II).

At this point we reasoned, due to our previous observation¹ and present success, that direct irradiation of a mixture of alken-1-ol (21 and 22) and PhSeSePh¹⁶ in the presence of 2 might lead to a one-pot sequential selenenylation and deselenenylation reaction. To this end, we irradiated a mixture of 21 (10 mM), 1 (5 mM), and 2 (1 mM) in methanol for 30 h, which gave 17 in 70% yield as the major product^{17,18} (Scheme II). A control experiment of 21 and 22 without 1 does not show any observable product, which is also supported from the insignificant fluorescence quenching of ¹DCN*. These results are coherent with the literature reports¹⁹ that only electron-rich olefins undergo electron-transfer processes

(16) PhSeSePh does not absorb any light under the present experimental conditions.

(17) 12 as the primary photoproduct was confirmed from the partial photolysis of 21 for 8 h: ¹H NMR (CDCl₃, 300 MHz) 7.45 (m, 2 H), 7.20 (m, 3 H), 3.94 (m, 1 H) 3.42 (m, 2 H), 3.01 (dd, 1 H, *J* = 7.2 and 12.2 Hz), 2.90 (dd, 1 H, *J* = 7.2 and 12.4 Hz), and 1.2-1.82 (m, 6 H); *m/e*⁺ 256, 172, 157, 85. This substantiates the sequential nature of the reaction.

(18) GC analysis of the crude reaction mixture also showed one small peak (<10-12%) which could be the methanol addition product of episelenonium cation.

(19) (a) Matty, J. *Angew. Chem., Int. Ed. Engl.* 1987, 26, 825. (b) Footnote h given in Table I.

with cyanoarenes. The most significant achievement of this finding has been the quantitative recovery of both PhSeSePh (97%) and DCN (98%) after the reaction. Further mechanistic and synthetic aspects of this reaction are in progress.

Acknowledgment. B.B.V.S.S. thanks the CSIR for financial assistance.

Preparation and Electronic Characterization of M₂(CCR)₄(PMe₃)₄: A Class of Conjugated Transition-Metal Complexes

Timothy C. Stoner, Richard F. Dallinger,[†] and Michael D. Hopkins*[‡]

Department of Chemistry, University of Pittsburgh
Pittsburgh, Pennsylvania 15260

Received March 5, 1990

Conjugated organic molecules and polymers comprise an extensive and fundamentally important class of molecules for which there is not a comparably developed and well-defined counterpart in transition-metal chemistry.¹ The dearth of such metal-containing analogues is surprising in view of the fact that their logical building blocks, namely, complexes that contain multiple metal-ligand² or metal-metal³ bonds, are known in abundance and are well-characterized structurally and electronically. Our interest in conjugated metal complexes was motivated by the belief that the incorporation of multiply bonded transition-metal centers into the backbone of an unsaturated organic chain should, given the widely tunable optical properties of metal complexes and the relative ease with which they support open-shell electronic configurations, significantly enhance the diverse physical properties possessed by conjugated organic molecules; dyes,⁴ conducting polymers,^{5,6} and carbon-based nonlinear optical materials^{6,7} are

[†]PRF Summer Research Fellow. Permanent address: Department of Chemistry, Wabash College, Crawfordsville, IN 47933.

[‡]NSF Presidential Young Investigator (1987-1992); Camille and Henry Dreyfus New Faculty Awardee (1987-1992).

(1) Molecular and electronic structural analogies between metal complexes and conjugated organic molecules are discussed in the following: Wheeler, R. A.; Hoffmann, R.; Strähle, J. *J. Am. Chem. Soc.* 1986, 108, 5381-5387.

(2) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley: New York, 1988.

(3) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*; Wiley: New York, 1982.

(4) Zollinger, H. *Color Chemistry*; VCH: New York, 1987.

(5) Skotheim, T. A., Ed. *Handbook of Conducting Polymers*; Marcel Dekker: New York, 1986.

(6) Prasad, P. N., Ulrich, D. R., Eds. *Nonlinear Optical and Electroactive Polymers*; Plenum: New York, 1988.

(7) (a) Hann, R. A., Bloor, D., Eds. *Organic Materials for Nonlinear Optics*; Royal Society of Chemistry: London, 1989. (b) Chemla, D. S., Zyss, J., Eds. *Nonlinear Optical Properties of Organic Molecules and Crystals*; Academic Press: Orlando, 1987.