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Redox-Mediated Decarboxylative Photo-Phenylselenenylation of N-Acyloxyphthalimides

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Decarboxylative phenylselenenylation of N-acyloxyphthalimides by visible light irradiation in aqueous solvents using catalytic amount of $Ru(bpy)_3Cl_2$ as a sensitizer in the presence of one equivalent of **BNAH** and 0.5 equivalent of diphenyl diselenide efficiently proceeds via redox-mediated radical chain mechanism. The **AIBN**-induced thermal reaction is also described.

Phenylselenenyl group is a versatile functional group in organic synthesis. Introduction of this useful functional group can be achieved typically by nucleophilic attack of phenylselenate anion or by reactions of carbanions with one equivalent of diphenyl diselenide or phenylselenenyl bromide.1) Radical addition method, in principle, can be carried out using only 0.5 equivalent of diphenyl diselenide, provided that phenylselenenyl radicals produced by S_H2 processes are effectively converted to diphenyl diselenide via radical coupling or more complicated redox-processes. However, the execution of this method is not simple matter and is thought to be strongly dependent on radical generation methods. Even in the excellent Barton's reaction which uses *O*-ester of thiohydroxamic acid derivatives and proceeds in very high quantum yields,2a) two equivalent of diphenyl diselenide is employed.2b) We have recently developed a new method of radical generation using N-acyloxyphthalimides,3) which can be easily prepared from carboxylic acids in high yields.4) This method may be applicable to such phenylselenenylation since N-acyloxyphthalimides are inactive to phenylselenenyl radical produced by S_H2 processes. We here report that the decarboxylative phenylselenenylation of N-acyloxyphthalimides effectively proceeds with use of only 0.5 equivalent amount of diphenyl diselenide. The reaction is performed in high chemical and quantum yields (>1.0) by visible light excitation in aqueous solvents via redox-mediated radical chain mechanism.

Irradiation of a THF-water (7:3, 40 ml) solution of N-acyloxyphthalimide (**1a**, 200 mg), 1-benzyl-1,4-dihydronicotinamide (**BNAH**)5) (118 mg, 1 equiv), and diphenyl diselenide (85 mg, 0.5 equiv) in the presence of a sensitizer $Ru(bpy)_3Cl_2$6) with visible light (>460 nm from a 500-W Xenon lamp) under a nitrogen atmosphere for 1 h produced the decarboxylated alkyl phenyl selenide (**2a**) in 85% yield along with phthalimide (87% yield). The reaction is general for various primary, secondary, and tertiary carboxylic acid derivatives. The yields are usually higher than 70% (Table 1). Although various solvents can be used in these reactions, THF is a superior solvent in viewpoint of the solubility of **1**.7) Furthermore, several light sources such as projector lamp or halogen lamp can be used. Table 1 also includes the results of exposure to sunlight. These reactions proceed via radical chain mechanism as recognized by the quantum yield values of some N-acyloxyphthalimides (**1a**, **1b**, and **1c**). Scheme 1 represents a possible reaction mechanism. As shown in our previous studies,3) the initial step of the reaction involves the electron transfer from **BNAH** to the excited state

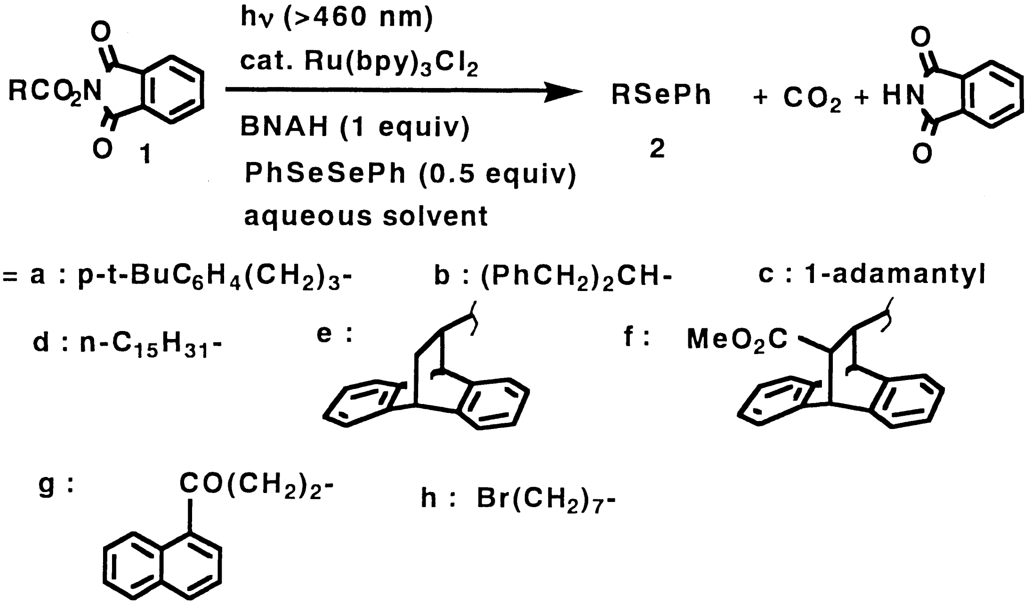
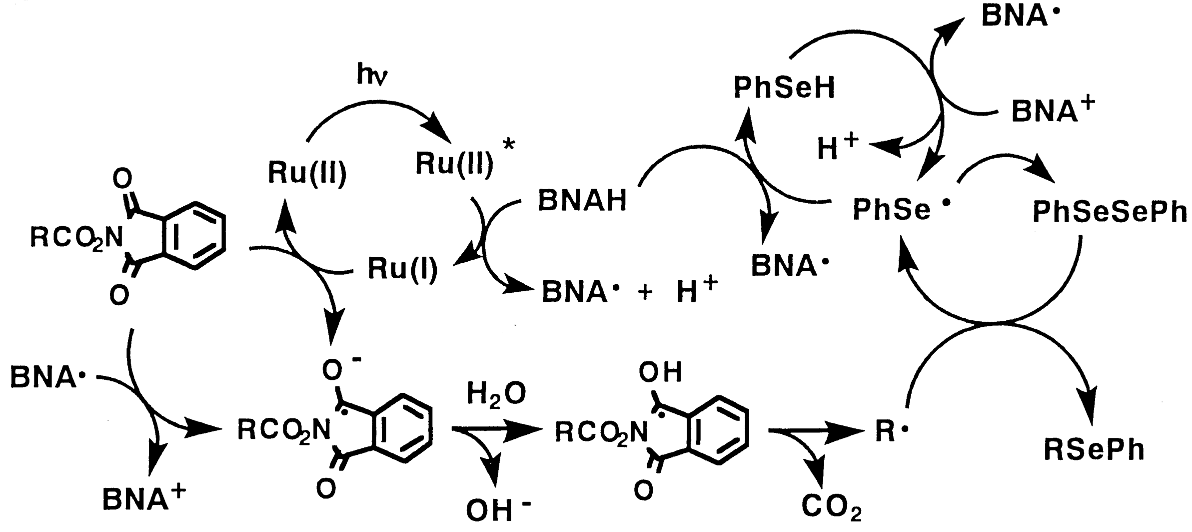


Table 1. Reductive Photodecarboxylation of N-Acyloxyphthalimides via Redox-Initiated Radical Chain Mechanism

Compound	Solvent (7:3)	Light source (time)	Yield of **2** /%	Quantum yield
1a	THF-H_2O	Xenon (1 h)	85	1.9
1a	acetone-H_2O	Xenon (1 h)	83	-[a)]
1a	THF-H_2O	sunlight (4 h)	81	-[a)]
1a	CH_3CN-H_2O	Xenon (1 h)	73	-[a)]
1b	THF-H_2O	Xenon (1 h)	89	3.8
1b	THF-H_2O	sunlight (1 h)	70	-[a)]
1b	THF-H_2O	projector lamp (1 h)	80	-[a)]
1b	acetone-H_2O	halogen lamp (1 h)	85	-[a)]
1c	THF-H_2O	Xenon (1 h)	84	2.0
1d	THF-H_2O	Xenon (1 h)	80	-[a)]
1e	THF-H_2O	Xenon (1 h)	86	-[a)]
1f	THF-H_2O	Xenon (1 h)	85	-[a)]
1f	THF-H_2O	sunlight (4 h)	86	-[a)]
1g	THF-H_2O	Xenon (1 h)	70	-[a)]
1h	THF-H_2O	Xenon (1 h)	67[b)]	-[a)]

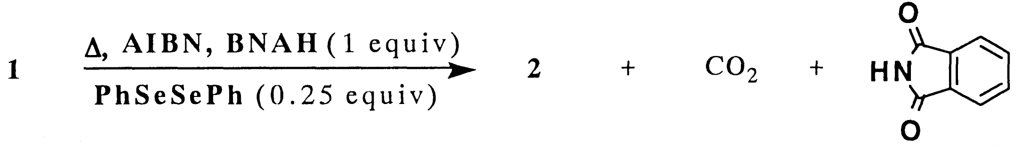
a) Not determined. b) 1,7-Di(phenylselenenyl)heptane was produced in 11%.

of Ru-sensitizer.[8,9] Both of the produced $Ru(bpy)_3^+$ and **BNA** radical can reduce **1** to give finally the decarboxylated radical. The radical adds to diphenyl diselenide to afford the desired decarboxylated selenide **2** and phenylselenenyl radical by the S_H2 process. The phenylselenenyl radical may dimerize or may abstract hydrogen from **BNAH** to give **BNA** radical (chain mediator) and selenophenol. Selenophenol may be oxidized under the conditions to regenerate diphenyl diselenide.[10] The formation of selenophenol may be supported by the following results; 1) the bromo functional group of **1h** is in part substituted by phenylselenenyl group during photolysis to give 1,7-di(phenylselenenyl)heptane, 2) the reaction also proceeds under the thermal conditions in the presence of small amount of **AIBN** as discussed in the next paragraph.



Scheme 1.

Table 2. Thermal Decarboxylative Phenylselenenylation of **1**[a)]



Compound	Solvent	Time /h	AIBN (equiv)	**2** /%	Recovery of **1** /%
1a	CH_3CN	1	0.25	53	0
1b	CH_3CN	1	0.10	80	0
1b	C_6H_6	20	0.50	25	67
1b	$THF-H_2O$ (40:1)	3	0.25	21	54
1b	$ClCH_2CH_2Cl$	10	0.50	14	-[b)]
1c	CH_3CN	1	0.25	68	17
1d	CH_3CN	1	0.25	55	7
1e	CH_3CN	1	0.25	57[c)]	-[b,c)]
1f	CH_3CN	1	0.25	71	0

a) Benzyl phenyl selenide is formed (3-15%) in all cases. b) Not determined. c) A rearranged selenide, 4-*exo*-phenylselenenyl-[2,3:6.7]-dibenzobicyclo[3.2.1]octa-2,6-diene is formed (16%).

When an acetonitrile (20 ml) solution of **1** (ca. 200 mg), **BNAH** (1 equiv), and diphenyl diselenide (0.5 equiv) is refluxed in the presence of a small amount of **AIBN** under a nitrogen atmosphere, **2** is produced in moderate yields (Table 2). The reaction is highly solvent dependent and acetonitrile is the best solvent examined; this is probably ascribed to the electron transfer from **BNA** radical to **1**. Under the conditions, **BNA** radical decomposes into nicotinamide and benzyl radical and a small amount of benzyl phenyl selenide is always formed. The fact that **2** is produced more than twice amount of added **AIBN** would be rationalized by assuming hydrogen abstraction path of phenylselenenyl radical from **BNAH**; thus the mechanisms of both thermal and photochemical reactions are compatible.

In comparison of the photochemical reactions with the thermal reactions, the photochemical reactions are much cleaner than the thermal reactions; for example, no formation of benzyl phenyl selenide and no rearrangement for **1e** were observed. Since phenylselenenyl group is readily converted into various functional groups such as halides, ethers, olefins, and so on, this method clearly widens the scope of synthetic methods starting from carboxylic acids.

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1) For instance, see; C. Paulmier, "Selenium Reagents and Intermediates in Organic Synthesis," Organic Chemistry Series, Volume 4, ed by J. E. Baldwin, Pergamon Press, Oxford (1986), pp. 84-123, and references cited therein.

2) a) D. H. R. Barton, P. Blundell, and J. C. Jaszbereni, *J. Am. Chem. Soc.*, **113**, 6937 (1991); b) D. H. R. Barton, D. Bridon, and S. Z. Zard, *Tetrahedron Lett.*, **25**, 5777 (1987); *Heterocycles*, **25**, 449 (1987).

3) K. Okada, K. Okamoto, and M. Oda, *J. Am. Chem. Soc.*, **110**, 8736 (1988); K. Okada, K. Okamoto, and M. Oda, *J. Chem. Soc., Chem. Commun.*, **1989**, 1636; K. Okada, K. Okamoto, N. Morita, K. Okubo, and M. Oda, *J. Am. Chem. Soc.*, **113**, 9401 (1991); K. Okada, K. Okubo, N. Morita, and M. Oda, *Tetrahedron Lett.*, **33**, 7377 (1992).

4) T. W. Greene, "Protective Groups in Organic Syntheses," John Wiley, New York (1981), p. 183; **1a-h** were easily prepared by mixing carboxylic acids with N-hydroxyphthalimide (1 equiv) in the presence of DCC (1 equiv) in CH_2Cl_2.

5) D. Mauzerall and F.H. Westheimer, *J. Am. Chem. Soc.*, **77**, 2261 (1955).

6) I. Fujita and H. Kobayashi, *Ber. Bunsenges.*, **76**, 115 (1972).

7) Water content in these mixed solvents is not important; 30%-water system was chosen simply because of its high water content and its reasonable solubility of **1**.

8) The redox-system of $Ru(bpy)_3Cl_2$-**BNAH** has been used by several reserchers; C. Pac, Y. Miyauchi, O. Ishitani, M. Ihama, M. Yasuda, and H. Sakurai, *J. Org. Chem.*, **49**, 26 (1984) and references cited therein; K. Hironaka, S. Fukuzumi, and T. Tanaka, *J. Chem. Soc., Perkin Trans. 1*, **1984**, 1705.

9) The conceivable electron transfer from the excited Ru-sensitizer to **1** is endothermic (ca. 12 kcal/mol) and in fact the luminescence of Ru-sensirzer is inefficiently quenched by **1a** in degassed acetonitrile ($k_q\tau<20$ M^{-1}), whereas the luminescence is known to be effectively quenched by **BNAH** ($k_q\tau=294$ M^{-1}).[8]

10) We tentatively assume that the oxidizing agent(s) would be **BNA**$^+$ or **Ru(II)**.

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