Photoinduced Electron Transfer (PET) Promoted Cross-coupling of Organoselenium and Organosilicon Compounds: a New Carbon–Carbon Bond Formation Strategy[†]

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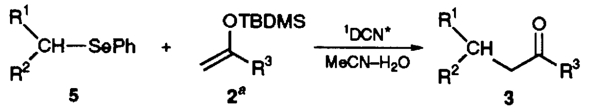
PET promoted cross-coupling of organoselenium compounds and silyl enol ethers is reported.

Carbon–carbon bond-forming reactions are the most fundamental and important in organic chemistry, and hence there has always been scope for development of newer strategies in this area of research. The cross-coupling of silyl enol ethers with aldehydes, Michael acceptors and S_N1 active alkyl halides, catalysed by Lewis acids, have been extensively utilised for C–C bond-forming reactions.[1–5] However, analogous coupling with non-activated primary or secondary alkyl halides has been found to be rather difficult, though moderate success has been recorded recently[6] utilising expensive silver acetate as catalyst. We have recently demonstrated[7] the activation of organoselenium compounds as carbocation equivalents, in contrast with their well-established utilisation as carbanion and radical equivalents,[8] by PET activation in aqueous solvent (MeCN : H_2O 4 : 1) employing the singlet excited state of 1,4-dicyanonaphthalene (^{1}DCN*) as electron acceptor. Facile nucleophile assisted cleavage of $[C\text{–}Se]^+$, formed by one-electron oxidation of organoselenium substrates, has led to the introduction of nucleophiles such as methanol onto the carbon. However, the introduction of carbon nucleophiles by PET oxidation of such compounds has remained unexplored. We predicted that PET activation of a mixture of organoselenium compounds and silyl enol ethers would lead to efficient cross-coupling of the two components and thus result in a new and unprecedented strategy for C–C bond formation.

It is known[9,10] that the selectivity of radical ion generation from a mixture of potential electron donors depends upon the magnitude of ΔG_{ET} values associated with the electron transfer processes. Therefore, PET activation of a mixture containing organoselenium substrate **1** and silyl enol ether **2** ought to selectively lead to the generation of $\mathbf{1}^{+\cdot}$ owing to the slightly more positive half-wave potential ($E_{\frac{1}{2}}^{ox}$ 1.70 V)[11] for oxidation of **2** (ΔG_{ET} −10.8 kcal mol^{-1})[‡] than for **1** (ΔG_{ET} *ca.* −13.0 kcal mol^{-1}).[7] Assisted cleavage of $\mathbf{1}^{+\cdot}$ with **2**, in S_N2 fashion as shown in Scheme 1, leads to the formation of the coupling product **3**. Phenylselenyl radical (PhSe), produced during the cleavage of $\mathbf{1}^{+\cdot}$, quickly dimerises to produce PhSeSePh.[12] $DCN^{-\cdot}$ generated in the process is transformed back to DCN through an established cycle[13] (Scheme 1) involving oxygen and water molecules and therefore making the whole reaction sequence 'truly photosensitised'. Effective C–C bond formation, utilising **2** as a carbon nucleophile, has also been reported[11] recently by trapping the electrophilic species generated during the anodic oxidation of α-heteroatom-substituted organostannanes. However, the scope of this approach is limited only to molecules equipped with an α-heteroatom bonded to C–Sn, an essential feature required to lower the oxidation potential of organostannanes to enable them to undergo anodic oxidation.

A typical reaction procedure consists of the irradiation (Pyrex filter, >280 nm, 450 W Hanovia medium pressure lamp, all light absorbed by DCN only) of a mixture containing **1** (2.5 mmol), **2** (2 mmol) and DCN (0.2 mmol) in MeCN–H_2O (4 : 1) solvent for 8–10 h, without removing the dissolved air from the reaction mixture. The reaction progress was monitored by GC (10% SE-30, 10 × 1/8″) analysis. After *ca.* 70% loss of **1**, photolysis was discontinued. Evaporation of the solvent followed by column chromatography (silica gel, 60–120 mesh) and purification of the reaction mixture afforded coupling products **3** (60–72%) and PhSeSePh, along with quantitative recovery of DCN (98%).[13] Results with a variety of organoselenium substrates and silyl enol ethers are given in Table 1. It is evident from these data that the present strategy of cross-coupling is quite general for C–C bond formating reactions, and is synthetically useful. However, the attempt to couple organoselenium compounds of type **5vi–vii** failed; this may be attributed to the strong stabilisation provided by the arene ring to the corresponding $[C\text{–}Se]^{+\cdot}$. To broaden the scope of this strategy for the formation of cyclic compounds, intramolecular couplings of C–Se bonds with a

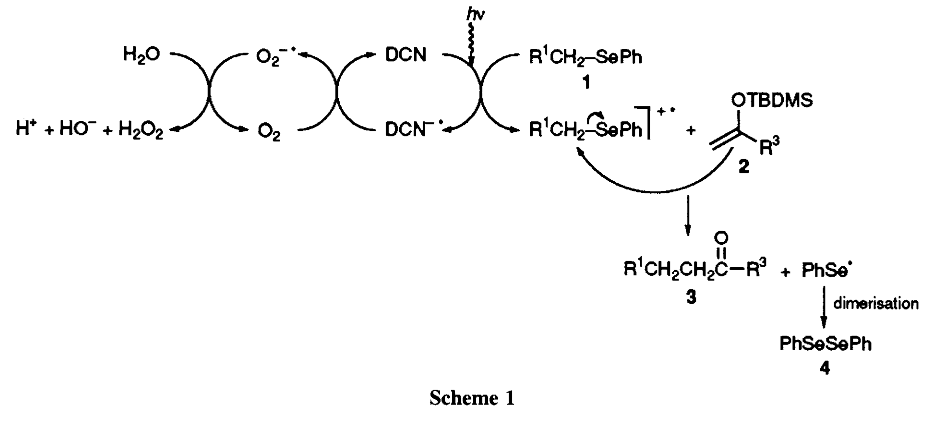
Table 1 PET promoted cross coupling reaction of organoselenium and organosilicon compounds



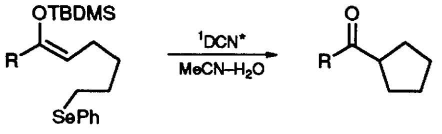
5 + **2**[a] → **3**

i	R^2 = n-C_7H_{15}, R^1 = H, R^3 = Ph	70%[b]
ii	R^2 = Me, R^1 = H, R^3 = Ph	72%[b]
iii	R^2 = $H_2C{=}CH_2$, R^1 = H, R^3 = Ph	65%[c]
iv	R^2 = $H_2C{=}CH_2$, R^1 = H, R^3 = Me	60%[c]
v	R^2 = n-C_7H_{15}, R^1 = H, R^3 = Me	62%[c]
vi	R^2 = Ph, R^1 = CO_2Et, R^3 = Me	ND[d]
vii	R^2 = Ph, R^1 = H, R^3 = Me	ND[d]

[a] Prepared by following the procedure reported in ref. 15. [b] Isolated yields, calculated based on 70% loss of **5**. [c] GC yield estimated by using internal standard. [d] ND = not detected.



Scheme 1



7
a R = Ph
b R = Me

8
80%
78%

Scheme 2

silyl enol ether moiety utilising compounds **7a–b** were attempted. These substrates were synthesised (70%) by stirring a mixture of the corresponding ketone, triethylamine, *tert*-butyldimethylsilyl chloride (TBDMS-Cl) and sodium iodide in MeCN at room temp. for 0.5 h.[14] PET activation of these substrates as described for **1**, followed by usual purification, gave the cyclised products **8a–b** (Scheme 2) in (78–80%) yield.

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Footnotes

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‡ ΔG_{ET} values were calculated from the Weller equation (D. Rehm and A. Weller, *Isr. J. Chem.*, 1970, **8**, 259), using $E_{\frac{1}{2}}^{red}$ for DCN -1.28 eV and $E_{0,0} = 3.45$ eV values as reported by us (ref. 7), 1 cal = 4.184 J.

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11 Oxidation potential values for silyl enol ethers are presumed to be in the range of 1.710 V as reported in J. I. Yoshida, M. Itoh and S. Isoe, *J. Chem. Soc., Chem. Commun.*, 1993, 547 for cyclohexyl silyl enol ether.
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