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Intramolecular Nucleophilic Addition of Silylenol Ether to Photosensitized Electron Transfer (PET) Generated Arene Radical Cations: A Novel *Non-Reagent* Based Carboannulation Reaction:

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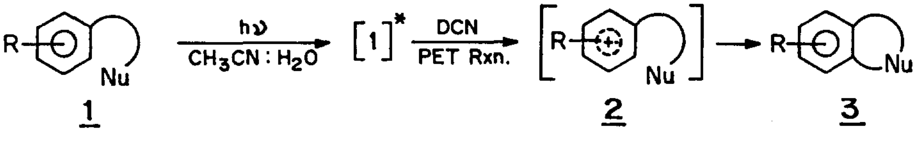
Abstract: *A New carboannulation strategy by intramolecular addition of silylenol ether to PET generated arene radical cation is reported.*

Carboannulation processes are among the most important reactions in organic synthesis[1]. Among the strategies reported for aromatic annulation reactions, the Friedel-Crafts type electrophilic substitution reactions[2] and electrocyclisations of *o*-quinodimethanes[3] have been the most common. More recently, addition of radical to arene rings[4] and Pd(II) catalysed diene reaction with aryl halides[5] have also been reported. Considering the importance of carbocyclization reactions, formulating a new strategy, incorporating latent functionality, is always desirable. In this context our attention was drawn towards the possible utilization of intramolecular nucleophilic substitution of aromatic rings with proximate carbon nucleophiles involving arene radical cation intermediate. Although aromatic nucleophilic substitution reactions involving aromatic radical cations[6-8] have been reported, their utilization as intermediates in carboannulation reactions have remained unexplored. Our spectacular success[9] in promoting the intramolecular nucleophilic addition of -OH and -NH_2 groups to PET generated arene radical cation **Scheme-I** led us to envision addition of proximate silyl enol ether[10] to arene radical cation for carbocyclisation purposes. We are pleased to disclose our preliminary result in this communication.

SCHEME-I



DCN = 1,4-dicyanonaphthalene

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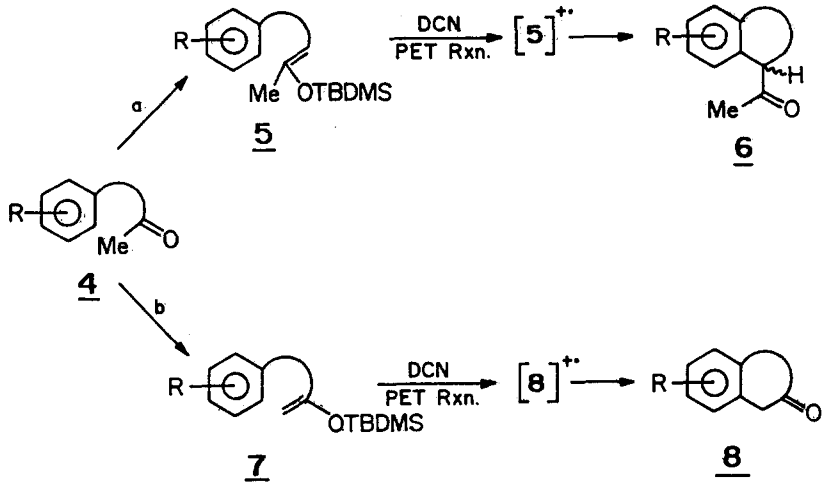
From starting compound 4, two different types of silyl enol ether (5 and 7) can be obtained by following the reported[11] experimental procedures for the synthesis of thermodynamic and kinetic silyl enol ethers, respectively. Therefore, cyclisations of these ethers are expected to produce two different types of carbocyclic compounds varying in ring sizes from the same ketone as shown in **Scheme - II.**

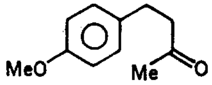
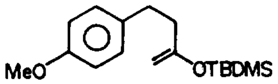
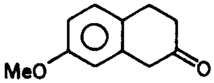
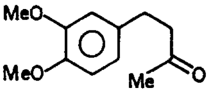
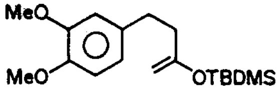
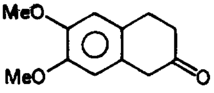
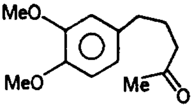
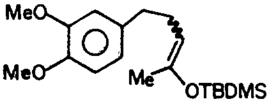
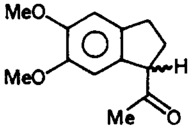
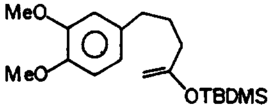
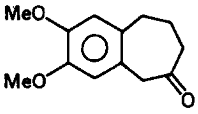
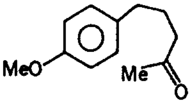
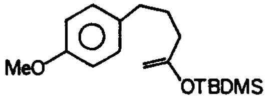
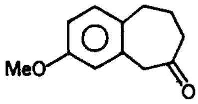
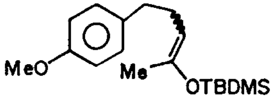
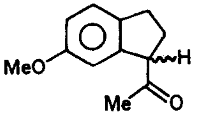
SCHEME-II



a = TBDMS·Cl , ImH, DMF, Δ, 48h
b = LDA, THF, -78°C, TBDMS·Cl, 3h

Silylenol ethers of type 5 are prepared in about 83 % yield by heating a mixture of 4 (5 mmol), TBDMSCl (6 mmol) and imidazole (12 mmol) in DMF (10 ml) for 48h followed by the usual workup, while those of type 7 are synthesized quantitatively (98 %), by the reaction of TBDMSCl (6 mmol) on the lithium enolate of type 4 (5 mmol) generated by the reaction of LDA at -78°C. A typical photochemical reaction procedure consist of the irradiation of a mixture of silylenol ethers (2 mmol) and DCN 0.06 g (0.34 mmol) in 500 ml of $CH_3CN:H_2O$ (4:1) for 3-4 h through pyrex filtered light (>280 nm all light absorbed by enolether only) using 450-W Hanovia lamp without removing the dissolved oxygen. Removal of the solvent and chromatographic purification of the reaction mixture gave carbocyclic products 19-24 (65-74 %). DCN was recovered quantitatively (98 %) at the end of the reaction[12]. During the irradiation of silylenol ethers of type 7, minor quantity (~10%) of starting ketones 4 are also formed which has been shown to be formed by the thermal reversion of 7 by adequate control experiment. Generality of the strategy have been shown by studying a number of carboannulation reactions as depicted in **Table - I.**

TABLE - I : Photoinduced Electron Transfer Promoted Carboannulation Reactions

	Ketone	Silyl Enol Ether[a]	Irrn. Time h	Product[b]	Yield[c] (%)
	 9	 13	3	 19	72
	 10	 14	3	 20	74
	 11	 15	4	 21	70
	"	 16	4	 22	74
	 12	 17	4	 23	65
	"	 18	4	 24	70

a) Silyl enol ethers 15 and 18 are the mixture of E and Z isomers and have been used as such (b) Characterised by ^{1}H NMR, ^{13}C NMR and mass spectral data. (c) yields not optimised.

The regiospecificity of these cyclizations are in accordance with the calculated electron densities (Huckel or MNDO) at different carbons of the HOMO of the arene radical cations as observed earlier[12].

In conclusion, we have demonstrated a novel carboannulation strategy which is flexible enough to incorporate amenable functionality. The attractive feature of this strategy lies in its ability to alter the ring size of carboannulated product from a single starting compound.

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