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Visible Light Initiated Photosensitised Electron Transfer (PET) Reductive β-Activation of α, β-Unsaturated Ketones for Radical Cyclisation: A new Concept in Promoting Radical Reactions

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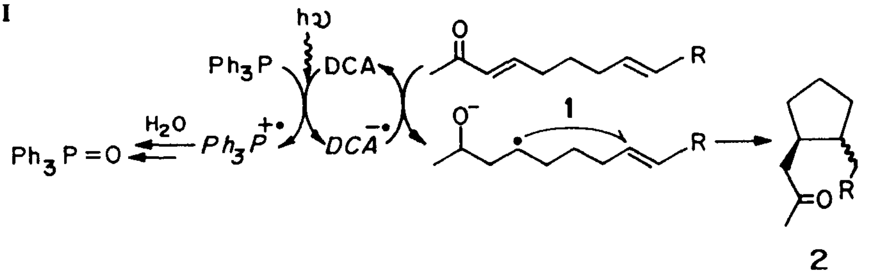
Abstract: *Photosensitised one electron reductive β-activation of α, β-unsaturated ketones for radical cyclisations are reported.*

The formation of carbon-carbon bond using free radicals have culminated in adding new dimensions to the repertoire of synthetic organic chemists[1]. Although carbon centered radicals for cyclisation are normally generated by reductive cleavage of -C-X (X = halogen, SPh, or OR) bond by Bu_3SnH, significant progress have also been made recently for promoting radical reactions by the use of transition metal compounds[2]. However, all these strategies for radical generation either use toxic reagents or produce toxic chemical wastes. In this present era of increased ecological concern and the requirement of clean and atom economy technology in chemical syntheses, it is mandatory on the part of organic chemists to find alternative strategy to initiate radical chemistry. In this endeavor, we have developed an unprecedented strategy for the β-activation of α, β-unsaturated ketones for radical cyclisation reactions by photosensitised electron transfer (PET) promoted one electron reductive processes from a photosystem, consisting of DCA (9,10-dicyanoanthracene) as visible-light harvesting electron acceptor and Ph_3P as sacrificial electron donor as shown in **Scheme-I**.

SCHEME - I



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The feasibility of sequential electron transfer processes from the above photosystem have been demonstrated[3] by estimating exergonic free energy change (ΔG_{et} = -47.25 KJM^{-1}) from the redox potential of

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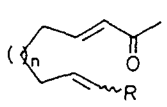
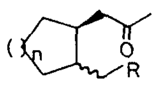
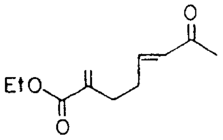
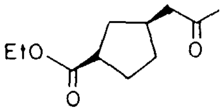
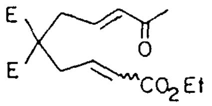
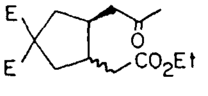
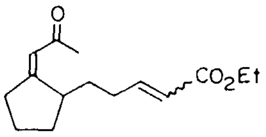
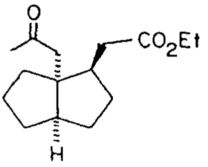
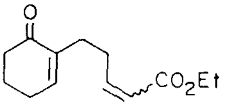
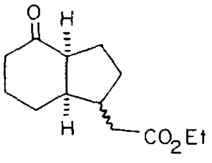
TABLE-I Photosensitised one electron reductive cyclisation of α,β-unsaturated ketones.

ENONES	PRODUCT[a]	YIELD (%)[b] (trans / cis)[c]
 1 a n=1 , R = COOEt b n=1 , R = CN c n=2 , R = CN d n=2 , R = COOEt	 2	 98 (85 : 15) 97 (80 : 20) 94 (68 : 32) 95 (75 : 25)
 3	 4	90 (40 : 60)
 5	 6	96 (80 : 20)
 7		92 (90 : 10)
 9	 10	93 (85 : 15)

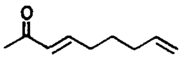
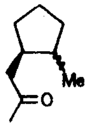
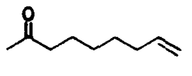
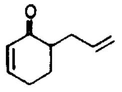
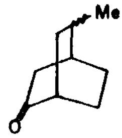
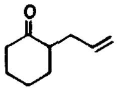
[a] Characterised by ^{1}H NMR, ^{13}C NMR and Mass spectral data; [b] Isolated yield; [c] Ratio determined by capillary GC (50 mts, methyl silicone) analysis.

DCA$^{\cdot}$(-0.89eV)[4] and **1a** (-0.40 eV)[5] by the equation $\Delta G_{et} = E^{1/2}_{oxd} - E^{1/2}_{red}$. The details of electron transfer processes from Ph_3P to $^1DCA^*$ and the efficient transformation of $Ph_3P^{+\cdot}$ to Ph_3PO have already been discussed by us previously[6].

A typical experimental procedure for β-activation of α,β-unsaturated ketones for radical reactions consists of the irradiation of a mixture of **1a** (3.60 mmol), Ph_3P (2.1 mmol), DCA (1.4 mmol) in DMF: i-PrOH: H_2O (88:10:2) in Pyrex tubes in argon atmosphere through filtered light from $CuSO_4.5H_2O$-NH_3 filter solution (405 nm)[7] using 450W Hanovia medium pressure lamp. After considerable (99%, 28h) disappearance of starting enone **1a**, the solvent was removed. Usual silica gel column-chromatographic purification of crude mixture gave the radical cyclised product **2a** in 17:3 ratio[8] with the major diastereomer having a *trans*-configuration[9]. Ph_3PO was formed as side product and DCA was recovered quantitatively (>98%). The cyclised products **2a** have been characterised by ^1H NMR, ^{13}C NMR and mass spectral data. The quantum yield (Φ)[10] of 0.011 for the formation of **2a** indicates that the product is not arising through the radical chain reaction.

To test the generality of this radical cyclisation strategy, a number of α,β-unsaturated ketones (1, 3, 5, 7 and 9) tethered with activated olefin were irradiated in the similar manner as described for **1a** and the results are listed in **Table-I**.

We also extended this strategy to examine the cyclisation of enones **11** and **14** possessing non-activated alkene acceptors. Unlike earlier reports[9], these compounds did undergo cyclisation to produce cyclised products **12** and **15** , albeit in slower rates and the cyclisations were accompanied with the enone reduction products **13** and **16**.

ENONES	PRODUCTS[a,b]	YIELD[c] (%)
 **11**	 **12**  **13** 70 : 30	55
 **14**	 **15**  **16** 68 : 32	50

[a] Characterised by ^1H NMR, ^{13}C NMR and mass spectral data.
[b] Ratio obtained by capillary GC column (50 mts, methyl silicone)
[c] Isolated yields, referred to only cyclised product **12** and **15**.

In conclusion, we have demonstrated a new concept in initiating radical reactions by β-activation of α,β-unsaturated ketones for intramolecular radical cyclisation by PET promoted one electron reductive processes. Further application of this reaction is in progress.

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5. Redox potential of 1 was measured from cyclic voltametry (Bioanalytical system, model CV-27).The cell consisted of a Pt inlay (working electrode), Ag/AgCl (referrence electrode), and Pt-wire as auxiliary electrode. Tetraethyl ammonium per chlorate in DMF was utilised as supporting electrolyte and potentials are referred to SCE. The DMF solution was degassed by argon bubbling for 10 minutes before measurements.
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8. The ratio was measured by capillary GC (methyl silicone, 50 mts) analysis.
9. The only analogy to such cyclisation may be found from the work of Enholm etal [Enholm, E. J. and Kinter, K. S. *J. Am. Chem. Soc.*, **1991**, *113*, 7784.] by employing O-Stannyl allylic radical intermediate from 1.
10. Quantum yield have been measured using Applied Photophysics Quantum Yield Train. Light intensity has been estimated using uranyl oxalate as chemical actinometer and product formation by HPLC (Perkin Elmer 135-c, Diode Array Detector) analysis using C_8 reverse phase column.
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