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PHOTOSENSITIZED SINGLE ELECTRON TRANSFER INITIATED N-DEBENZYLATION. A CONVENIENT AND MILD APPROACH

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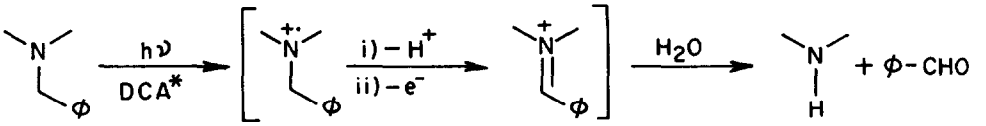
Abstract: A mild method of N-debenzylation via photosensitized single electron transfer (SET) using 9,10-dicyano anthracene (DCA) as electron acceptor in neutral medium is reported.

Benzylation is an effective way of protecting amines in the synthesis[1] of complex molecules, but its deprotection has been severely often limited. Previous methods have involved either traditional high pressure catalytic hydrogenation[2,3] or formic acid[4] and other hydrogen donors[5]. The mild approach of using β-trimethyl silyl chloroformate[6] for deprotection also lacks general adaptability as it requires very low temperatures (-50°C) and toxic phosgene gas for reagent preparation. In another related study we observed the photosensitized SET generation of appropriate iminium cation from exciplex dissociation of amine-^{1}DCN* and its intramolecular cyclization by oxygen or carbon nucleophile[7]. This easy approach of generating iminium cation prompted us to report a convenient and mild method for N-debenzylation via iminium cation hydrolysis (Scheme-I). Singlet excited state of 9,10-DCA[8] ($E_{1/2}$-0.89eV, $\Delta E_{0,0}$2.88eV)[9] has been utilized as electron acceptor for these reactions.



SCHEME-I

An acetonitrile:water (7:3) solution containing benzylated amines (1.85×10^{-2}M) and DCA (8.3×10^{-5}M) in pyrex tubes are irradiated by 450-W Hanovia lamp at 405 nm, isolated by using $CuSO_4$:NH_3 solution filter for 6-10 hr. The irradiation time could considerably be reduced by broad band irradiation using uranium yellow filter (> 350 nm) or irradiating in Rayonet reactor fitted with 3500 Å lamps. Further marked increase in the deprotection rate could be achieved by increasing the pH (≈12 pH) of the solvent. The results are summarised in Table-I.

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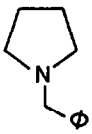
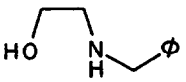
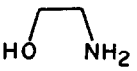
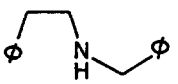
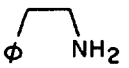
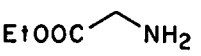
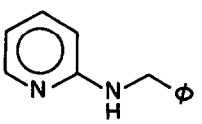
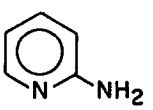
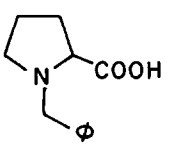
TABLE I – SET INITIATED N-DEBENZYLATION

Entry	Substrate	Product	Yield[a,b] (%)	K_q ($m^{-1}s^{-1}$)[c]
1			90	1.33×10^{10}
2			80	1.04×10^{10}
3			80	1.3×10^{10}
4			78	1.13×10^{10}
5			75	2.8×10^{10}
6		—		No quenching[d]

(a) Isolated yield; (b) yields were not optimized; (c) estimated by fluorescence quenching Stern Volmer plot analysis of $^1DCA^*$ ($\lambda_{excit.}$ 420 nm) by benzylated amines; (d) Fluorescence quenching and deprotection was not observed as free amino acids exist in the Zwitterionic form in aqueous solution.

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