### PHOTOSENSITIZED SINGLE ELECTRON TRANSFER OXIDATION OF N-HYDROXYLAMINES: A CONVENIENT SYNTHESIS OF CYCLIC NITRONES

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Abstract: Photolysis of N-hydroxylamines of type 1 in the presence of 1,4-dicyanonaphthalene (DCN) as an electron acceptor gave high yields of nitrones 2. Crude nitrones have been trapped by 1,3-dipolar cycloaddition reaction with dimethyl fumarate. Mechanistic pathways have also been discussed.

Photoexcited aromatic hydrocarbons form exciplexes with amines<sup>1-3</sup>. Since the exciplexes are more polar than the uncomplexed excited aromatic hydrocarbons, it is well known that exciplexes dissociate into ion-pairs or ion radical pairs in polar solvents<sup>1-3</sup>. There have been enough efforts made in rationalizing the competition between energy and electron-transfer in amine aromatic hydrocarbon pairs, either as bimolecular or intramolecular systems<sup>4,5</sup>. Lewis recently discussed in detail the selectivity of N-H vs & -CH transfer from amines to arenes via a singlet exciplex, in polar as well as nonpolar solvents<sup>6,7</sup>. The observation of products in organic systems from primary electron transfer to amines also depends on the feasibility and selectivity of *c*-CH bond dissociation.

The cyclic nitrones 2 are valuable intermediates (1,3-dipoles) for constructing various biologically active nitrogen heterocycles<sup>8</sup>. Although there are methods<sup>9</sup> for synthesizing nitrones 2



from  $\underline{1}$  including the most recent one<sup>10</sup>, they lack the convenient feasibility, either because of methodology<sup>10</sup> or owing to the requisite of using excess of oxidising agent and troublesome work-up procedure<sup>9</sup>. With our continuing interest in photoinduced single electron transfer (SET)



reaction<sup>11,12</sup>, we report herein the easy and convenient synthesis of <u>2</u> from N-hydroxylamines (<u>1</u>) by photoinduced SET reaction using  ${}^{1}\text{DCN}^{*}$  as an electron acceptor.

A 4:1 (V/V) acetonitrile water solution containing N-hydroxypiperidine (3, 10 mM) and 1,4-dicyanonaphthalene (5.6 mM) was irradiated through a pyrex filter (>280 nm) using a 450-W Hanovia medium pressure lamp at room temperature for 4 h. The nitrone  $\underline{4}$  was isolated in 90% yield: Its physical and spectral characteristics were identical to the values reported earlier<sup>9,10</sup>. It should be noted that 4 was the only product observable on TLC.

The fluorescence of DCN is quenched by <u>3</u>. A value of Kq (1.24 x  $10^{10}$  M<sup>-1</sup>S<sup>-1</sup>) was obtained from the least square slope of a fluorescence quenching Stern-Volmer plot taking a singlet lifetime of 10.1 ns for DCN in acetonitrile<sup>13</sup>. The observation of diffusion controlled quenching for the reaction of <sup>1</sup>DCN<sup>\*</sup> and <u>3</u> is indicative of excited donor-acceptor (EDA) stabilised exciplex<sup>14</sup>. The free energy change for exciplex formation ( $\Delta G_{ex}$ ) calculated from the Weller equation<sup>15</sup> gave the endoergic value of -1.40 eV<sup>16</sup>.

The exciplex of <sup>1</sup>DCN<sup>\*</sup> and <u>3</u> dissociates into the ion-radical pairs in acetonitrile : Water solvent, which upon  $\measuredangle$ -C-H deprotonation followed by subsequent steps as shown in Scheme I resulted in nitrone  $\frac{4}{4}$ <sup>17</sup>.



#### SCHEME I

Since the isolation of nitrones is not always necessary for their utilization as 1,3-dipoles, crude nitrones have been trapped by heating with dimethyl fumarate in an inert atmosphere to give five-membered heterocyclic compounds<sup>18</sup>. Table I illustrates some of the examples.



# Table I : 1,3-Dipolarcycloaddition of nitrones, generated by photosensitized SET reaction, with Dimethyl fumarate.

- a) N-Hydroxylamines were prepared by the method reported  $^{\ensuremath{\mathsf{I}}\,\ensuremath{\mathsf{9}}}.$
- b) Adducts characterised by IR, <sup>1</sup>H NMR and mass spectra and confirmed by comparing with reported values<sup>9,10</sup>.
- c) Isolated yields. No attempts were made to quantify individual isomers.

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- Energy of excitation and reduction potential for DCN have been taken from Arnold's work<sup>13</sup>, 0.68 eV vs. SCE was the value used for the oxidation potential of 3<sup>10</sup>.
- 17. The DCN could be recovered unchanged in 98% at the end of the reaction. The DCN<sup>-\*</sup> formed by accepting electron from hydroxylamines decays back to DCN in the following manner.

## [DCN<sup>-</sup>· protonation H-DCN oxid DCN]

For more details and examples see, M.A. Fox "Advances in photochemistry", D.H. Volman, K. Gollnick and G.S. Hammond (Ed.), John Wiley & Sons, Vol. 13, 237 (1986).

- 18. After irradiation, equimolar amount of dimethyl fumarate was added to the photolysed mixture and contents refluxed for 2 h in the presence of argon gas. Removal of the solvent and normal column chromatography over silica gel (Merck, Kieselgel 60, 230-400 mesh) gave pure 1,3-dipolar cycloadducts using hexane : EtOAc (9:1) as eluent.
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