

# Oxoisoaporphines: Regioselective deuterium labelling involving the metastable hydrogenated photoproduct anions

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During the  $^1\text{H}$  NMR study of the photoreduction of aza-oxoisoaporphines, aza-OIAs, (7H-benzo[e]perimidin-7-ones) by amines we found an unexpected H/D isotopic exchange in the aromatic positions 4 and 6 of these molecules. This surprising exchange motivated us to probe it with previously studied oxoisoaporphines, OIAs, (1-aza-benzo[de]anthracen-7-ones) and 2,3-dihydro-oxoisoaporphines, 2,3-dh-OIAs, (2,3-dihydro-7H-dibenzo[de,h] quinolin-7-ones). All of these compounds photoreduce efficiently in the presence of aliphatic tertiary amines through a stepwise mechanism of electron-proton-electron transfer. This photoreaction generates an AH<sup>-</sup> anion hydrogenated either at the N-atom, for 2,3-dh-OIAs, or at the O-atom for aza-OIA and OIAs. These long-lived metastable photoproducts revert thermally to the initial oxoisoaporphines nearly quantitatively. In the presence of D<sub>2</sub>O, regioselective exchange of the aromatic protons at positions 4 and 6 takes place to an extent greater than 90% under very