Trimethylsilyl-Induced N–O Bond Cleavage in Nitrous Oxide-Derived Aminodiazotates

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Upon chemical activation, nitrous oxide (N₂O) typically acts as a clean O-atom transfer reagent with dinitrogen as the benign byproduct.[1] Utilization of N₂O as an N-atom donor, on the other hand, has received much less attention. For such purposes, both nitrogen- and carbon-based nucleophiles have been explored but with only limited success, except for N-heterocyclic carbenes (NHCs) which form stable covalent adducts with N₂O and can be further functionalized into azo dyes, with the azo group originating from N₂O.[1] Recently, we have found that lithium dialkylamides, for example lithium diisopropylamide, readily capture N₂O to give metastable lithium dialkylaminodiazotates.[2] These diazotates undergo N–O Bond Cleavage when treated with Grignard reagents, preserving the N atoms from N₂O in the trisubstituted triazenes products, the latter of which represent highly useful reagents in synthetic organic chemistry. In this study,[3] we demonstrate that N-trimethylsilyl (TMS)-substituted amides can also form covalent adducts with N₂O. The resulting aminodiazotates undergo spontaneous N–O bond cleavage, giving inorganic or organic azides accompanied with Si–O bond formation. N-TMS-substituted amide was also found to effect N–O bond cleavage in N₂O-derived dialkylaminodiazotates, generating unsymmetrical tetrazene monoanion salts. These results indicate the potential of TMS in devising N₂O transformations where value-added N-containing chemicals can be obtained.