Diversification of ammonium salts via α-ammonio radical

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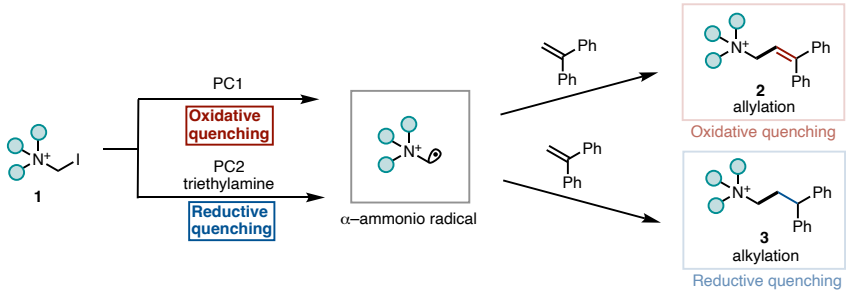
Nitrogen-containing compounds, especially quaternary ammonium salts, are ubiquitous in various high-value materials, such as pharmaceuticals, agrochemicals, and catalysts. However, the preparation of these compounds is limited to the reactions of tertiary amines. If ammonium salts can be converted into other ammonium salts, the discovery of novel classes of potential bioactive molecules can be accelerated. Herein, we report new synthetic methods for the preparation of these compounds through diversification of quaternary ammonium salts.[1)] The key active species in our reactions is the distonic α-ammonio radical, which is generated via photoredox catalysis (PC). Notably, we achieved the generation of α-ammonio radical by two different mechanisms of PC: oxidative quenching and reductive quenching.

Two types of radical generation mechanisms allowed us to control products of reactions between ammonium salt **1** and olefins. Under oxidative quenching conditions, ammonium salt **1** is direct one electron reduced by PC, and allylation occurs to afford product **2**. On the other hand, under reductive quenching conditions, triethylamine is one electron oxidized by PC, and generated radical abstracts iodine atom from ammonium salt **1**, thus, this condition produces alkylation product **3**.[2)] These two types of products are produced efficiently with high selectivity. This procedure was applied to the derivatization of bioactive quaternary ammonium salts and tertiary amines, spiro-cyclic ammonium salts, and the identification of salinity-tolerance-conferring molecules.



1) Kinoshita T.; Sakakibara, Y.; Hirano, T.; Murakami K. *Chem* in press. DOI:10.1016/j.chempr.2024.11.004
2) Constantin, T.; Leonori, D. *et al. Science* **2020**, 367, 1021–1026.