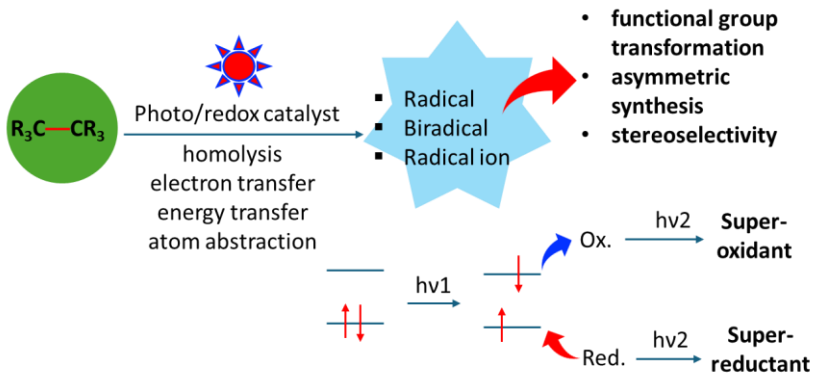
1-7-1. Organic Photoreactions Involving Radicals, Biradicals, and Radical Ions

Overview

In organic photoreactions, radicals, biradicals, and radical ions emerge as key intermediates through homolysis or electron transfer processes originating from excited states generated upon light absorption. These photoinduced intermediates are highly reactive, driving bond cleavage and the formation of new bonds. For example, biradicals formed via excited carbonyl species contribute to cyclization and rearrangement reactions, enabling efficient skeletal transformations. On the other hand, radical ions produced through photoinduced electron transfer facilitate precise redox processes, and in recent years they have been widely applied to C–C bond formation and C–H functionalization via photoredox catalysis.

Current Status and Frontiers

Radicals generated by photo-induced homolysis or hydrogen atom transfer have long been exemplified by classical Norrish reactions and photo-halogenations. In recent years, radical generation under mild conditions using visible-light photoredox catalysts (Pac et al.), organic dyes,



and semiconductor photocatalysts has become mainstream, enabling C–C bond formation, C–H activation, and decarboxylative couplings. Advances in continuous-flow photoreactors and machine-learning-based optimization have promoted scalable synthesis, paving the way toward industrial application. Furthermore, ConPET (consecutive photoinduced electron transfer, Wenger) and highly reducing photocatalysts have opened access to activating otherwise inert aryl C–F and C–Cl bonds (König). The integration of sustainable catalyst design with reaction engineering will be key in the future.

Biradicals, readily formed from triplet-excited carbonyl compounds, are exemplified by Norrish type II reactions and [2+2] photocycloadditions. Recently, triplet–triplet energy transfer

has enabled precise control of cycloadditions under visible-light conditions, expanding applications to stereoselective synthesis. Particularly, the use of photoenzymes in radical reactions represents a breakthrough, achieving stereocontrol that was previously unfeasible (Hyster). Advances in theoretical calculations and ultrafast spectroscopy are clarifying mechanisms, establishing molecular design principles based on energy-transfer efficiency and distance dependence. Re-examination of classical Norrish mechanisms has also deepened understanding of side reaction control and type selectivity.

Radical ions produced by photoinduced electron transfer (PET) open up precise redox pathways, enabling C–C bond formation, deprotection, and functionalization. Two recent directions are noteworthy: first, electron donor–acceptor complexes, which allow direct electron transfer upon photoexcitation of donor–acceptor assemblies without metal catalysts; second, the use of PET and two-photon excitation to achieve super-reducing potentials, enabling visible-light activation of previously challenging substrates. In addition, hybrid catalytic systems that merge electrochemistry and photochemistry, as well as electrocatalysis, are being developed to reconcile energy efficiency with scalability (Lin; Shirakawa).

References

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Future Perspectives and Directions

Organic photoreactions mediated by radicals, biradicals, and radical ions are predicted to advance toward greater precision and sustainability. In radical chemistry, super-reducing photocatalysts and flow photochemistry will expand transformations of otherwise challenging substrates. Biradical chemistry will progress through photoenzymes and triplet energy transfer, enabling refined stereocontrol and asymmetric synthesis. Radical ion chemistry will be driven by EDA complexes and electro–photochemical hybrids, providing low-energy, high-efficiency access to diverse substrate transformations.

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