

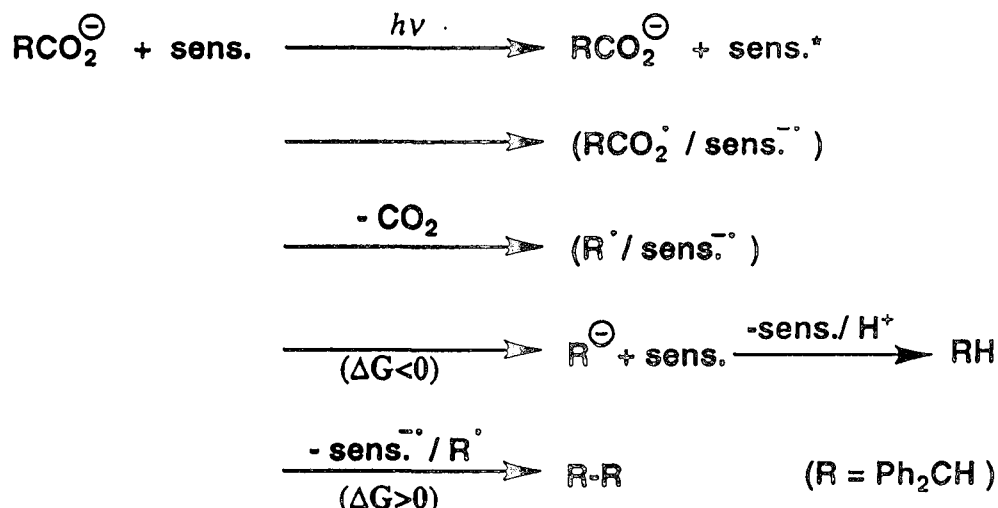
Persistent Radical Ion Effect in Photoinduced Electron Transfer Reactions of Radicals

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A) Redox Reaction of Carboxylates to Yield Carbanions

Photo-Kolbe reaction of carboxylates is known to yield the corresponding decarboxylated radicals. We have found that the photochemical redox reaction of arylcarboxylates in the presence of electron-attracting sensitizer. Thus, the irradiation of diphenylacetate ion in the presence of cyanoaromatics such as cyanonaphthalene yielded the corresponding carbanion.



When the reduction of radical is favorable, i.e., exothermic, the formation of diphenylcarbanion (450 nm) was the major reaction. The carbanion formation was shown to proceed in the solvent cage since the reduction was the major one even in the presence of oxygen. The reaction rate of the carbanion with oxygen and methanol could be determined.

When the radical reduction is unfavorable (i.e., endo-thermic) as in the presence of dicyanoanthracene (DCA), the corresponding radical (325 nm) could be observed by the conventional laser spectroscopy. In this case, DCA radical anion was accumulated and could reduce the carbon radical to carbanion slowly.