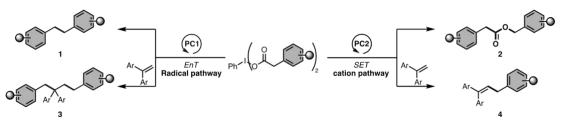
Decarboxylative transformation modulated by photocatalyst

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Carboxylic acids are abundant and readily available starting material. The recent development of photoredox catalysts, which can induce single-electron transfer (SET) under visible light irradiation, has enhanced the utility of carboxylic acids as an alkyl radical precursor.¹ Because of the inherent nucleophilic nature of alkyl radicals, various electrophilic substrates can react with carboxylic acid under photoredox-conditions. Recently, reactions between carboxylic acid and nucleophilic substrates were attained.² In these reactions, carbocations are utilized as key intermediates, which generate via photoredox-catalyzed radical-polar crossover mechanism from carboxylic acid. During the course of our study^{2a}, we envisioned that the control of these distinct reactive intermediates by the choice of photocatalyst (PC) would offer an opportunity to develop divergent decarboxylative reactions that give different products from the same starting materials.

Herein, we report a photocatalyzed divergent decarboxylative transformation of arylacetic acids activated by hypervalent iodine. Our reaction enables the divergent synthesis of 1,2-diarylethane 1 and arylmethyl arylacetate 2 from arylacetic acids. The divergency of our decarboxylation is derived from two distinctive reaction pathways of photocatalytic triplet excited state: energy transfer (EnT) and SET. With a catalyst that favors EnT, C–C bond formation proceeds via the radical-radical coupling. Under SET conditions, on the other hand, benzyl cation is a reactive intermediate that generates through the radical-polar crossover mechanism, and C–O bond formed product is obtained. Additionally, by adding 1,1-diaryl ethylene as a reactant into our optimal conditions, dibenzylated product 3 or monobenzylated product 4 were obtained with good selectivity by changing the photocatalyst, respectively.



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