

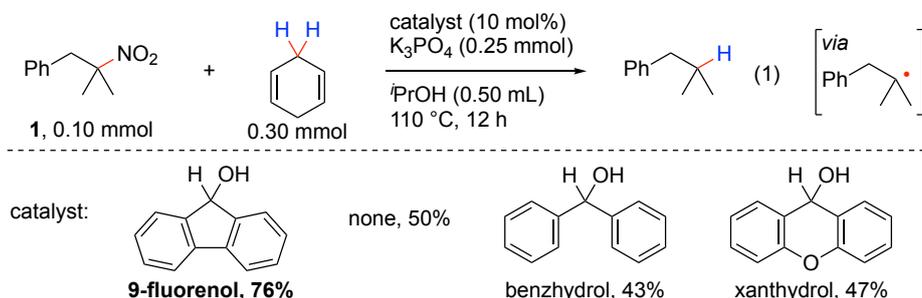
9-Fluorenol-Catalyzed Denitrative Radical Generation from Nitroalkanes

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Nitroalkanes are useful synthetic intermediates to construct complex molecules. Their highly acidic α -proton enables α -functionalization of them through deprotonation followed by the reaction with electrophiles under mild conditions.¹ Despite obvious benefits of denitrative transformations, however, reductive removal of a NO₂ group from nitroalkanes is still difficult because of competitive reduction of the NO₂ group itself to give nitroso compounds, hydroxylamines, and amines. Conventional denitration relied exclusively on the use of tin hydride (Bu₃SnH in most cases),² which is accompanied by some drawbacks such as toxicity of organotin compounds, trouble in separation, and functional group tolerance. In this context, a less toxic, inexpensive, easy-to-handle, and ideally catalytic substitute for tin hydride is of high demand to make the most of synthetic utility of nitroalkanes. We hypothesized that the C–NO₂ bond cleavage is induced by single-electron transfer (SET) from a non-oxophilic reductant, which is reluctant to abstract oxygen atom from radical anions of nitroalkanes.³

It turned out that the reductive denitration of nitroalkane **1** was efficiently catalyzed by 9-fluorenol in the presence of 1,4-cyclohexadiene as a hydrogen atom donor, K₃PO₄ as a base, and solvent *i*PrOH as a terminal reductant (eq. 1). Although the reaction gradually proceeded in the absence of 9-fluorenol, other alcohols such as benzhydrol and xanthydrol did not improve the efficiency, indicating the importance of a planar fluorene skeleton. The use of Michael acceptors instead of 1,4-cyclohexadiene afforded the corresponding alkylated products as well. The present system outperforms the conventional method using tin hydride in terms of cost, safety, and experimental manipulation.



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