One-step Direct Oxidation of Alkoxy to Ketone for Evaporable Fullerene-fused Ketone as Efficient Electron-transport materials

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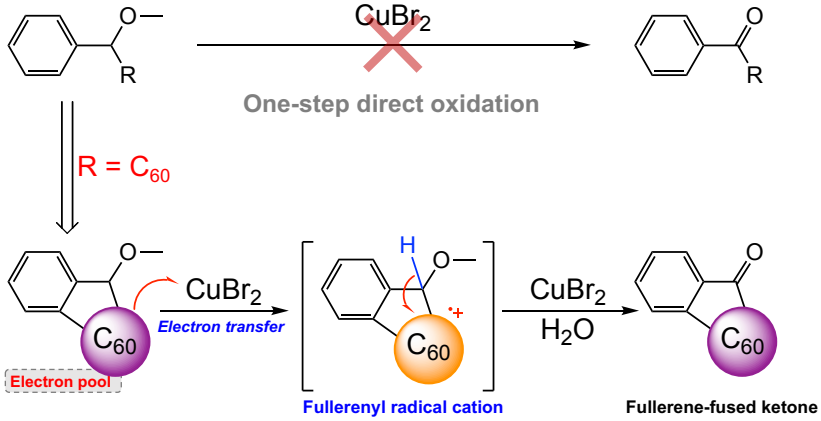
Keywords: One-step Oxidation; Alkoxy Groups; Fullerene Redox Pendant; Fullerene-fused Ketones; Evaporable Fullerenes



Oxidation reactions, such as the direct oxidation of alcohols to aldehydes or ketones, are among the most critical and fundamental transformations in organic synthesis. However, the oxidation methods are limited when alcohols are protected/functionalized with an alkyl group to form the alkoxy structure, which is mainly attributed to high activation energy barrier for directly converting the alkoxy group to ketone structure. Consequently, the one-step direct oxidation of alkoxy to ketone has yet to be presented. Fullerene, a well-known intrinsically electron-deficient molecule, is prone to accept electrons affording the reduced fullerene anion species for versatile functionalization. With our interest in exploring the classical organic chemistry reaction under assistance of fullerene, and also inspired by the recent studies on fullerene radical cation ($C_{60}^{\bullet+}$) mediated reaction, we conceived that $C_{60}^{\bullet+}$ should be feasible for the one-step oxidation of alkoxy group to ketone through the electron transfer activation. Herein, we report a copper (II) bromide promoted one-step direct oxidation of alkoxy to ketones with the aid of an oxidizable fullerene pendant. Distinct from the unfavorable energy barrier in direct oxidation of alkoxy group to ketone, fullerene pendant serves as an electron pool for facilitating the electron transfer from the alkoxy structure to oxidant. Mechanistic studies indicate that the fullerene assisted one-step oxidation involves two critical steps: 1) electron transfer from C_{60} to Cu[II] affords $C_{60}^{\bullet+}$, and 2) the generated $C_{60}^{\bullet+}$ attracts electron density from the neighboring C–H bond, contributing to the further electron transfer from the alkoxy structure to the fullerene cage. Meanwhile, obtained fullerene-fused ketones are fabricated to the electron-transport layers through thermally deposition, which provides the photovoltaic devices with uniformly pin-hole free electron-transport films. The reaction presented herein not only provides an understanding on one-step oxidation of alkoxy group to ketone, but also access the high-quality electron-transport layers through thermally evaporation.