

缺电子芳烃侧链基的光氧化

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摘要 研究了9,10-二氧蒽(DCA)和四氯对苯二醌(TCBQ)敏化的甲苯、对氯甲苯、对氯基甲苯和对硝基甲苯的电子转移光氧化反应。DCA和TCBQ均可敏化甲苯和对氯甲苯的光氧化。产物为相应的取代苯甲酸和取代苯甲醛。DCA和TCBQ均不能有效敏化对氯基甲苯和对硝基甲苯的光氧化,但在反应体系中加入与反应物等摩尔的联苯为共敏化剂后,两者即可顺利氧化为相应的取代苯甲酸和取代苯甲醛。通过荧光淬灭和共敏化剂联苯、无水盐高氯酸镁、O<sub>2</sub>捕获剂对苯二醌以及电子给体对二甲氧基苯等外加试剂对光氧化的影响讨论了反应历程。

关键词 苯甲醛 P 光敏化 反应机理 光氧化 甲苯 蒽 苯甲酸 P 氯甲基苯 四氯苯醌 电子转移反应 氧(基)络合物

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### Photoxidation of side chains of electron-deficient aromatic hydrocarbons

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**Abstract** The electron transfer photooxygenation of toluene, p-chlorotoluene, p-cyanotoluene, and p-nitrotoluene sensitized by 9,10-dicyanoanthracene (DCA) and chloranil were reported. Photooxygenation of toluene and p-chlorotoluene could be sensitized by DCA or chloranil, yielding the corresponding substituted benzaldehydes and benzoic acids as products. Neither DCA nor chloranil could sensitize the photooxygenation of p-cyanotoluene and p-nitrotoluene. However, both hydrocarbons could be photooxygenated in the presence of equimolar amount of biphenyl as cosensitizer and with chloranil as sensitizer to give the corresponding substituted benzaldehydes and benzoic acids. The reaction mechanisms were discussed according to the fluorescence quenching studies and the effects on the reaction of different additives such as cosensitizer biphenyl, O<sub>2</sub>-trap benzophenone, anhydrous salt Mg(ClO<sub>4</sub>)<sub>2</sub> and electron donor p-dimethoxybenzene.

**Key words** BENZALDEHYDE P PHOTSENSITIZATION REACTION MECHANISM PHOTOOXIDATION METHYLBENZENE ANTHRACENE BENZENECARBOXYLIC ACID P CHLOROMETHYLBENZENE CHLORANIL ELECTRON TRANSFER REACTION CYANO COMPLEX

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