

相转移催化反应研究 V: 利用¹⁴C标记法研究取代苯乙烯及 α -芳代苯乙烯与二溴卡宾反应动力学

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摘要 本文应用放射性计数进行反应物及产物的定量测定, 比较了一些冠醚类相转移催化剂的性能.

发现新型氮杂冠醚在催化二溴卡宾与1,1-二苯乙烯加成反应时有最好的催化性能. 本文还测定了取代苯乙烯、 α -芳代苯乙烯类化合物与二溴卡宾反应的相对速率常数, 并通过线性相关分析,

比较了两类化合物与二溴卡宾反应特性常数的差别, 对 α -取代苯乙烯中取代基R的性质和相对速率常数作了比较.

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Studies on phase transfer catalysis V: A kinetic study of the cycloaddition of dibromocarbene with substituted styrenes and α -arylstyrenes by ¹⁴C labelling method

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Abstract The relative rate constants k_{rel} of the PTC reaction of p-substituted styrenes I (R = H, Me, Cl, MeO, NO₂) with dibromocarbene were measured by radiocounting method and the k_{rel} values were analyzed by linear correlation method. The r_+ value of the PTC reaction of α -arylstyrenes II (R₁ = 3-Me, 4-Me, H, 3-Cl, 4-MeO, 3-CF₃) with dibromocarbene system was smaller than the one obtained from substituted styrene reaction. It was suggested that the aryl group of α -arylstyrene might disperse the pos. charge from a carbon atom. A variety of the crown compounds were used as PTC catalysts for the reaction of 1,1-diphenylethylene and dibromocarbene and it was found that N,N'-disubstituted azacrown possessed the highest catalytic activity for this reaction. Six 1-¹⁴C-1, 1-dibromo-2-aryl-2-phenyl-cyclopropanes were prepared and identified by comparison with the unlabeled authentic samples III which were characterized by elemental anal., NMR, MS, and TLC anal.

Key words [QUANTITATIVE ANALYSIS](#) [CATALYSIS](#) [REACTION KINETICS](#) [NITROGEN](#) [HETEROCYCLICS](#) [BROMINE COMPOUNDS](#) [CROWN ETHER COMPOUNDS](#) [LABELLED COMPOUNDS](#) [PHASE TRANSFER CATALYSIS](#) [CARBENE](#) [ELECTRONIC EFFECT](#) [ADDITION REACTION](#) [REACTION RATE CONSTANT](#) [STYRENE](#) [P](#) [RADIOACTIVITY](#) [CARBON ISOTOPES](#)

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