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亚烷基卡宾与丙烯环加成反应机理的理论研究

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摘要 用二阶微扰理论研究了单重态亚烷基卡宾与丙烯环加成反应的机理，采用 MP2/6-31G~*方法计算了势能面上各驻点的构型参数、振动频率和能量。根据所得 势能面上的能量数据可以预言，反应（1）的a途径和反应（2）的b途径将是单重态亚烷基卡宾与丙烯环加成反应的两条相互竞争的主反应通道，两反应途径均由两步 组成，(I)两反应物分别生成了富能中间体INT1a和INT2b，它们均是无势垒的放热 反应，放出的能量分别为60.28和26.33kJ·mol~(-1).(II)中间体INT1a和INT2b分 别通过过渡态TS1a和TS2b异构化为三元环产物P1和四元环产物P2，其势垒分别为 16.43和12.73kJ·mol~(-1)。

关键词 碳烯 环加成反应 势能面 过渡态 丙烯 微扰论 反应机理

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Theoretical Study on the Mechanism of the Cycloaddition Reaction between Alkylidene Carbene and Propylene

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Abstract The mechanism of cycloaddition reaction between singlet alkylidene carbene and propylene has been investigated with second-order Moller- Plesset perturbation theory. Using MP2/6-31G* method, geometry optimization, vibrational analysis, and energetic calculation have been done for the involved stationary points on the potential energy surface. According to the data of energy on the surface energy profile calculated, we predict that path a of the cycloaddition (1) and path b of cycloaddition (2) would be two major competition channels of the title cycloaddition between singlet alkylidene carbene and propylene, both proceeding in two steps: (I) the two reactants form two energy-rich intermediates INTla and BMT2b, which are exothermic reactions without energy barrier releasing 60.28 and 26.33 kj/mol, respectively; (II) two intermediates INTla and INT2b isomerize to a three-membered ling product (Pi) and a 4-membered ring product (P2) via transition states TSla and TS2b with energy barriers of 16.43 and 12.73 kj/mol, respectively.

Key words CARBENE CYCLOADDITION REACTION POTENTIAL ENERGY SURFACES TRANSITION STATE PROPENE PERTURBATION THEORY REACTION MECHANISM

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