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Changing the regioselectivity and asynchronicity of the possible concerted [2+2] and [4+2] cycloadditions of ketene and halogenated ketenes with cyclopentadiene: a DFT survey

Seyed Majid Musavi *, Javad Amani, Niku Omidian

Department of Chemistry, Shahr-e-Qods Branch, Islamic Azad University, Tehran 37515-374, Iran

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ABSTRACT

Two concerted Diels–Alder [4+2] and two concerted Staudinger [2+2] reactions between ketene and/or dihaloketenes with cyclopentadiene are examined at B3LYP/6-31+G* level. For the parent ketene, two cycloaddition modes including [2+2] across the C=C and [4+2] across the C=C bond of ketene are thermodynamically favorable (ΔE=−13.4 and −17.3 kcal/mol, respectively) while the two other including [2+2] across the C=O and [4+2] across the C=O bond of ketene are endoergic. The corresponding barrier heights change to a lesser amount and ranging from 20.8 to 35.1 kcal/mol. Halogenated ketenes significantly affect both the thermodynamics and kinetics of these reactions in a way that they increase the exoergicity and reduce the barrier heights result in the decrease of regioselectivity. Unsymmetrical bond formations in the structures of TSs indicate that all the reaction modes are concerted and synchronous but halogens increase the asynchronicity due to the electronic effects. Moreover, three transient halogenated cycloadducts obtained through the [4+2] cycloaddition across the C=O bond are converted to some new products via a [3,3] sigmatropic rearrangement. The AIM pictures show that in the [4+2] cycloadditions four TS structures represent pericyclic reactions, while all the [2+2] reactions are classified as pseudopericyclic. FMO theory is applied to justify the findings. The reliability of B3LYP results is confirmed through comparison with the HF and MP2 methods.

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1. Introduction

Cycloaddition reactions are some of the most powerful methods in the synthesis of cyclic and heterocyclic compounds mainly for those with pharmacological interest and also for the preparation of many natural products.[1,2] Four- and six-membered ring compounds are typically constructed by the well-known [2+2] and [4+2] cycloadditions.[3–5] Among many types of organic compounds, ketenes have received an extensive consideration owing to their ability to selectively participate π bonds in the commonly encountered [2+2] cycloaddition reactions with alkenes,[6,7] imines,[8,9] and azadienes.[10,11] On the other hand, the cycloaddition reactions of ketenes and dienes have achieved a distinctive status in organic chemistry due to their problematic nature and the unusual mechanistic pathways they follow.[12] In contrast to related compounds, such as allenes and heterocumulenes, most ketenes do not appear to react by the routine Diels–Alder cycloadditions; also, the ketenes react preferentially with olefins across the C=C bond rather than the C=O.[13–15] It was proposed that the [2+2] or [4+2] cycloadducts of ketenes can take place along a highly asynchronous concerted or a step-wise mechanism via a zwitterionic intermediate.[16,17] Moreover, the substituents on the diene and/or the dienophile play an important role in controlling the periselectivity observed in the cycloaddition reactions.[18] The ketene cycloadditions of cyclopentadiene (cp), known since the first decades of 20th century,[19,20] have provided useful insights into the mechanism of thermal [2+2] cycloaddition reactions. Subsequently, more than 65 ketenes with cp and 25 ketenes with 1,3-cyclohexadiene have been reported to afford cyclobutanones. However, Machiguchi et al.,[21–23] Singleton et al.,[24] and Roberts et al.[25] have recently shown that cyclobutanone is not the only product of these reactions and the situation is more complicated. The careful study of diphenylketene cycloaddition to cp conducted at low temperature resulted in the formation of a cyclic ether as the primary [4+2] product, while the expected cyclobutanone proposed to from via the rearrangement of the [4+2] reaction product at higher temperatures[24] (Scheme 1).

Similarly, in 1999 Machiguchi et al. noticed[22] that reaction of diphenylketene with 1,3-cyclohexadiene yields an ether as the primary product, which is then converted thermally into the cyclobutanone. However, the fact that 1,3-cyclohexadiene derivatives and diphenylketene give a mixture of [2+2] and [4+2] cycloadducts was

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* Corresponding author. Tel./fax: +98 21 46896519, +98 912 4801 243 (mobile); e-mail address: moosavi_majid@yahoo.com (S.M. Musavi).

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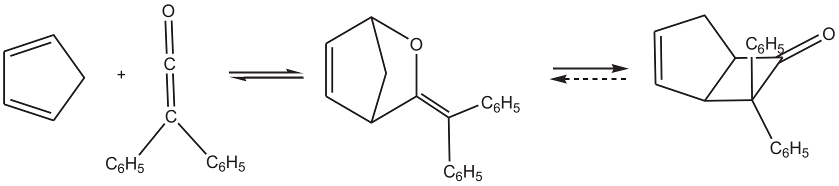
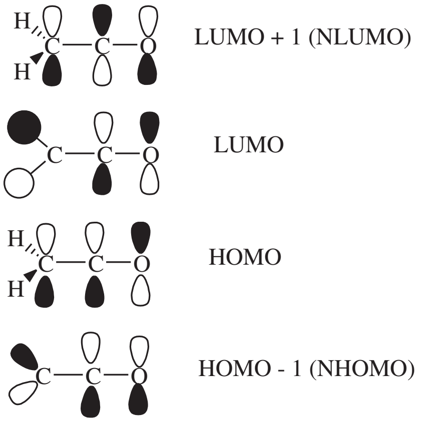


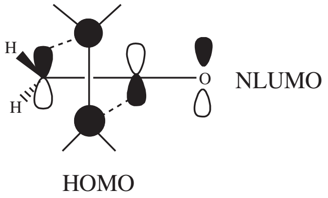
Scheme 1. The cycloaddition of diphenylketene with cp.

first documented by Roberts et al. in the early 90s.[25–28] In this ambiguous atmosphere, Singleton et al.[24] proposed that the computation of dynamic trajectories could shed light on the complex picture of the cp and diphenylketene cycloaddition. A molecular orbital MO overview of the ketene–cp cycloadditions may help understand those controversies.[29] The frontier MOs of ketene are as follows (Scheme 2).



Scheme 2. The frontier MOs of ketene.

Since the terminal carbon atom in the C═C bond of ketene is the site of a node in the lowest unoccupied molecular orbital (LUMO), the significant interaction of the second alkene component's highest occupied molecular orbital (HOMO) must be with the next available unoccupied MO (NLUMO) if bonding to that carbon is to be achieved (Scheme 3).



Scheme 3. MO presentation for interaction of ketene with alkene.

The regiochemistry in the cycloaddition between chloroketene and cp, which reacts to give a single [2+2] cycloadduct, is dictated by the large NLUMO coefficient on the ketene central carbon and a large HOMO coefficient on the terminal carbon of the diene (Scheme 4).

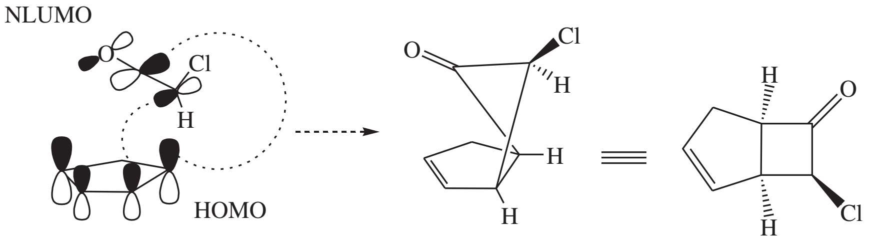
However, further studies indicated that an alternative approach is may be constructive at least for the case of diphenylketene and cp.[10] In this reaction mode, just the C═O bond of the ketene is involved in the first step, therefore the diene HOMO may usefully interact with the ketene LUMO. The ketene can orient itself with the large group away from the plane of the diene to result in a specific stereochemistry in the cycloadduct. Subsequent Claisen rearrangement (a [3,3] sigmatropic process, which is suprafacial in all components) gives rise to the same product that we predict on the basis of a [2+2] cycloaddition[30] (Scheme 5).

The purpose of this paper is to focus on the mechanistic and periselectivity of ketene cycloadditions. Hence, we present a detailed density functional theory (DFT) investigation on [2+2] and [4+2] cycloaddition reactions of ketene as well as dihaloketenes with cp at four pathways leading to all possible products (Scheme 6).

The effects of halogens on the thermodynamic and kinetic properties of ketene–cp cycloadditions are also the objectives in this survey. Our mechanistic predictions are based on several computational findings including the geometrical parameters and energetics throughout reactants→transition states (TSs)→cycloadducts, the intrinsic reaction coordinate (IRC) calculations, the atoms in molecules (AIM) analysis of critical points of the electron density in the TSs, and NBO analysis.

2. Computational details

Geometries and energies of all stationary points including reactants, TSs and products are fully optimized at hybrid density functional theory (DFT) using the GAUSSIAN 98 program suite.[31] The B3LYP method is shown to be quite reliable on both the geometries and energies of cycloaddition reactions.[32–34] The 6-31+G* basis set[35] is selected for all the atoms. Vibrational frequency calculations at the same level of theory for optimization are used to characterize all of the stationary points as either minima (the number of imaginary frequencies, NIMAG=0, or transition states, NIMAG=1). Natural bond orbital (NBO) calculations[36] are done at B3LYP/6-311++G**. The transition states (TSs) linking the initial and final structures are found using the reactants products quasi synchronous transient (QST2) algorithm.[37] The relative energies are, thus, corrected for vibrational zero-point energies (ZPE) and the transition states both to the reactant and the product directions in the reaction pathways are examined by using the intrinsic reaction coordinate (IRC).[38] The current electron densities corresponding to B3LYP/6-311++G** wave functions are employed for the AIM calculations by AIM 2000.[39,40]



Scheme 4. Regiochemistry in the cycloaddition between chloroketene and cp via MOs.

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