

[6 + 2] AND [4 + 2] CYCLOADDITION REACTION OF DIPHENYLKETENE AND CYCLOHEPTATRIENE

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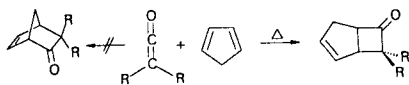
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Abstract

The cycloaddition reaction of diphenylketene and cycloheptatriene is studied. The reaction proceeds via a highly asynchronous reaction path to the zwitterionic **6** as intermediate. Subsequent CC-bond formation yields 8, 8-diphenylbicyclo [4. 2. 1] nona-2, 4-dien-7-one (**1**) and 7,7-diphenylbicyclo [3. 2. 2] nona-2, 8-dien-6-one (**2**) in a 1:1 ratio as formal [6+2] and [4+2] cycloaddition products.

Introduction

It is generally well-known that the reaction of ketenes with dienes results in the selective formation of [2+2] cycloadducts [1, 2]. Remarkably, the corresponding Diels-Alder products are not formed at all (eq. 1).



Equation 1

Based on the orbital symmetry control rules, Woodward and Hoffmann have provided an explanation for the exclusive formation of [2+2] products in the cycloaddition reaction of ketenes with dienes [3]. In agreement with these rules, a suprafacial, antarafacial $[2_s+2_a]$ cycloaddition mode accommodates, in an ideal way, steric and electronic interactions while preserving orbital symmetry [4]. Thus, as a

result of kinetic control, vinylcyclobutanones and not the thermodynamically more stable Diels-Alder products are formed.

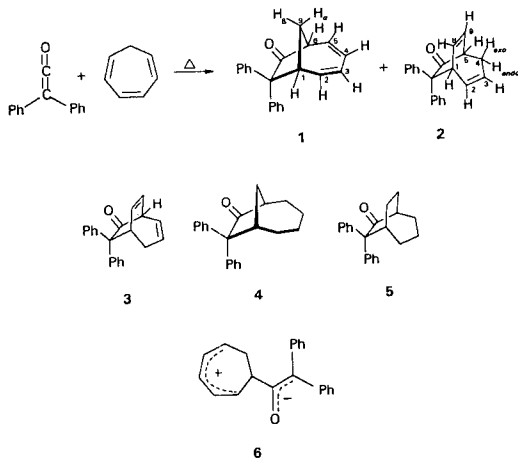
According to several recently published *ab initio* calculations at various levels of approximations, the simple picture provided by the Woodward-Hoffmann theory casts some doubt [5]. Most likely the cycloaddition proceeds via a highly asynchronous transition state.

In this connection, we present here an anomalous result which we observed several years ago during the study of cycloaddition reaction of diphenylketene with cycloheptatriene [6, 7].

Results and Discussion

Refluxing a solution of diphenylketene in cycloheptatriene (1:2) as solvent after 24 h leads with 17.5% yield to the [6+2] cycloadducts **1** and the formal Diels-Alder product **2** as a mixture of two isomers in a 1:1 ratio. Interestingly, in these reactions neither a [2+2] product nor alternatively the 6,6-diphenylbicyclo [3. 2. 2] nona-2, 8-dien-7-one (**3**) were formed.

Keywords: Diphenylketene; Cycloheptatriene; Diels-Alder reaction; Asynchronous cycloaddition



Formula 1

The structure assignment of **1** and **2** is based primarily on the spectral data and, especially in the case of **2**, on chemical shift experiments. In accordance with the structure, infrared spectra of compound **1** shows a carbonyl absorption at 1735 cm⁻¹ characteristic of cyclopentanone derivatives and compound **2** a carbonyl absorption at 1710 cm⁻¹. Furthermore, the ¹H NMR spectra (see experimental section) and the catalytically hydrogenation to the bicyclononanes **4** and **5** are in agreement with these structures.

The lack of [2+2] cycloaddition by the reaction of diphenylketene with cycloheptatriene or its valence isomer bicyclo [4. 1. 0] hepta-2, 4-dien, is surprising [8]. The formation of **1** and **2** is casually described *via* a highly asynchronous reaction path which leads ultimately to the electronically favorable pentadienyl cation **6** as intermediate and subsequent CC-bond formation yields the products **1** and **2**.

Experimental Section

8,8-Diphenylbicyclo [4. 2. 1] nona-2, 4-dien-7-one (**1**) and 7,7-diphenylbicyclo [3. 2. 2] nona-2, 8-dien-6-one (**2**)

A solution of 54 g (0.28 mol) of diphenylketene in 60 g (0.65 mol) cycloheptatriene is stirred under reflux for 25 h. Excess of cycloheptatriene is removed by careful distillation under vacuum and the residue is refluxed with 400 ml petroleum ether (40-60). Petro-

leum ether layer is separated and concentrated to 150 ml. The resulting oil is crystallized from ether to give 14 g (17.5%) mixture of **1** and **2** in a 1:1 ratio. The ratio of **1**:**2** is determined by comparing the carbonyl absorption in infrared spectra and the ¹H NMR spectra of the mixture. A probe of **1** and **2** could be separated by medium pressure chromatography (3 atm) over silica gel with a 8:2 mixture of petroleum ether (40-60) and CH₂Cl₂.

8,8-Diphenylbicyclo [4. 2. 1] nona-2, 4-dien-7-one (**1**)

¹H NMR (CDCl₃) δ = 2.04 (d, H-9α, J H-9, H-9β = 12.3 Hz), 2.72 (p, H-9β, J H-1, H-9β = 7.8 Hz, J H-6, H-9β = 6.5 Hz), 3.40 (m, H-1, J H-1, H-2 = 7.4 Hz, J H-1, H-6 = 2.6 Hz), 3.87 (m, H-6, J H-5, H-6 = 7.6 Hz), 5.44 (d, d, H-2, J H-2, H-3 = 11.5 Hz), 5.64 (dd, H-5, J H-5, H-4 = 11.0 Hz), 6.06 (dd, H-3, J H-4, H-3 = 10.5), (t, H-4) and 6.96-7.42 (m, 10H).- IR (KBr): ν = 1735 (C=O) cm⁻¹.

C₂₁H₁₈O (286.34) MS (70 eV): m/z = 286.

7,7-Diphenylbicyclo [3. 2. 2] nona-2, 8-dien-6-one (**2**)

¹H NMR (CDCl₃) δ = 2.32 (m, H-4exo, J H-4exo, H-4endo = 19 Hz), 2.59 (m, H-4endo), 3.12 (m, H-5, J H-6, H-6 = 6.0 Hz), 3.60 (m, H-1, J H-1, H-2 = 8.5 Hz, J H-1, H-7 = 7.0 Hz), 5.41 (m, H-3), 5.65 (m, H-2,

J H-2, H-3 = 6.0 Hz), 5.86 (m, H-6, J H-6, H-7 = 9.0 Hz), 6.66 (m, H-7), 7.36-7.64 (m, 10H). -IR (KBr): $\nu = 1710$ (C=O) cm^{-1} . -MS (70 eV): $m/z = 286$.

| | | | |
|---|-------|---------|--------|
| $\text{C}_{21}\text{H}_{18}\text{O}$ (286.34) | Calc. | C 88.07 | H 6.33 |
| | Found | C 88.20 | H 6.32 |

8,8-Diphenylbicyclo [4. 2. 1] nonan-7-one (4)

A solution of 50 mg **1** in 100 ml absol. ethanol is hydrogenated in the presence of Pd/C (10% C) at atm. pressure. After separation of the catalyst and solvent, the residue is crystallized from petroleum ether. 45 mg (90%) **4**, mp 153-155°C. -IR (KBr): $\nu = 1725$ (C=O) cm^{-1} . -MS (70 eV): $m/z = 290$.

| | | | |
|---|-------|---------|--------|
| $\text{C}_{21}\text{H}_{22}\text{O}$ (290.40) | Calc. | C 86.85 | H 7.63 |
| | Found | C 86.70 | H 7.76 |

7,7-Diphenylbicyclo [3. 2. 2] nonan-6-one (5)

A solution of 50 mg **2** in 100 ml absol. ethanol is hydrogenated in the presence of Pd/C (10% C) at atm. pressure. After separation of the catalyst and solvent, the residue is crystallized from petroleum ether. 45 mg (90%) **5**, mp 151-152°C. -IR (KBr): $\nu = 1705$ (C=O) cm^{-1} . -MS (70 eV): $m/z = 290$.

| | | | |
|---|-------|---------|--------|
| $\text{C}_{21}\text{H}_{22}\text{O}$ (290.40) | Calc. | C 86.85 | H 7.63 |
| | Found | C 87.02 | H 7.49 |

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