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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).

\[ \text{Equation 1} \]

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, antrafacial [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 \textit{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.
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 \(^1\)H 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). Petroleum ether layer is separated and concentrated to 150 ml. The resulting oil is crystalized 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 \(^1\)H 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 CH\(_2\)Cl\(_2\).

8,8-Diphenylbicyclo [4.2.1] nona-2, 4-dien-7-one (1)

\(^1\)H NMR (CDCl\(_3\)) \(\delta = 2.04 \) (d, H-9\(\alpha\), J H-9, H-9\(\beta\) = 12.3 Hz), 2.72 (p, H-9\(\beta\), J H-1, H-9\(\beta\) = 7.8 Hz, J H-6, H-9\(\beta\) = 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): v = 1735 (C=O) cm\(^{-1}\).

C\(_{22}\)H\(_{18}\)O (286.34) MS (70 eV): m/z = 286.

7,7-Diphenylbicyclo [3.2.2] nona-2, 8-dien-6-one (2)

\(^1\)H NMR (CDCl\(_3\)) \(\delta = 2.32 \) (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): ν = 1710 (C=O) cm⁻¹. - MS (70 eV): m/z = 286.

C₂₁H₁₈O (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): ν = 1725 (C=O) cm⁻¹. - MS (70 eV): m/z = 290.

C₂₁H₂₂O (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): ν = 1705 (C=O) cm⁻¹. - MS (70 eV): m/z = 290.

C₂₁H₂₂O (290.40)  
Calc. C 86.85  H 7.63  
Found C 87.02  H 7.49

**References**

6. After the MS Thesis of A. Saadatmandi (1977), (Sharif University of Technology, Department of Chemistry) we did not continue these studies. By exploring the literature, we recently discovered that G. A. Taylor et al. [7] have also studied the same reaction. Interestingly these workers only isolated the compound 2. Because the formation of the [6+2] product 1 is of special interest for these cycloaddition reactions, we publish our additional results here.