



Cyclodimerization reactions of the β -ferrocenylvinyl(methyl)ketones in the presence of zinc-organic compounds

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ABSTRACT

Trans-ferrocenyl-3-buten-2-one **1** undergoes cyclic dimerization with formation of 4-acetyl-3,5-diferrocenylcyclohexanone **5** and 5,8-diferrocenyl-1-hydroxybicyclo-[2.2.2]octan-3-one **6** in the presence of cyclohexenes and 2-PyZnBr or Me₂Zn. No adducts of the Diels–Alder reaction of compound **1** in its enolic form with cyclohexenes were observed. Under similar conditions, in the absence of cyclohexenes *trans*-ferrocenyl-3-buten-2-one **1** affords cyclodimer **5** and cyclotrimer – 6-acetyl-4,5,7-triferrocenyl-1,9-dehydro-2-decalone **7**. 3-(Ferrocenylmethylidene)pentane-2,4-dione **2a** and ethyl (*E*)-2-acetyl-3-ferrocenylacrylate **2b** cyclodimerized analogously with formation of 3,5-diferrocenyl-1-hydroxy-2,4,4-triacetylcyclohexene **8a** and diethyl 4-acetyl-3,5-diferrocenyl-1-hydroxycyclohexene-2,4-dicarboxylate **8b**, respectively. The structures of the obtained compounds were established based on data from IR, ¹H and ¹³C NMR spectroscopy, mass spectrometry and X-ray diffraction analysis. The mechanistic aspects of these reactions are discussed.

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1. Introduction

Compounds with ferrocene units and enone, endione, diene and polyene fragments have garnered the interest of researchers [1]. Ferrocenyl-substituted 1,3-dienes gained prominence by virtue of their exciting structures, chemical reactivity, and potential use as molecular building blocks and, in the realm of supramolecular chemistry, as redox-switching receptors [2–5].

The following methods are currently applied to access ferrocenylbuta-1,3-dienes: dehydration of ferrocenyl(alkyl)allylic alcohols [6–8], deprotonation of ferrocenyl(alkyl)allylic cations [6–9], and the Wittig reaction [10]. Ferrocenyl-, (aryl)ferrocenyl-, (alkyl)ferrocenyl-, (alkyl)diferrocenyl- and (aryl)diferrocenyl-1,3-dienes have been reported; their cationic cycloaddition [8,9], thermal [4 + 2]-cycloaddition Diels–Alder and thermal [4 + 2]-cyclodimerization [6,7] reactions occur with high diastereoselectivity. The reaction products comprise alkylaryl(ferrocenyl)-substituted six-membered carbocycles that are either free or fused to other carbo- or heterocyclic systems.

In most of these studies, 1,3-aryl(ferrocenyl)- or 1,3-alkyl(ferrocenyl)-2-propenones (chalcones) were used as initial

compounds for preparation of ferrocenylallylic alcohols, allylcations, and dienes. However, the study of the properties of ferrocenylchalcones as dienophilic, 1,3-heterodienic or 3-hydroxy-1,3-dienic systems remain largely unexplored. The literature reveals that ferrocenylchalcones were described as participants in Diels–Alder reactions, only in three papers [11–13]. All they describe their application in the presence of AlCl₃ as a dienophile.

Our goal was to study the possible reactivity of 4-ferrocenyl-3-buten-2-one [ferrocenylvinyl(methyl)ketone, chalcone], and its 3-acetyl- and 3-ethoxycarbonyl-analogs, as 4-ferrocenyl-2-hydroxy-1,3-butadienes in [4 + 2]-cycloaddition reactions in the presence of zinc-organic compounds. We hoped to determine optimal reaction conditions for the Diels–Alder cycloaddition reactions of the chosen ferrocenylvinyl(methyl)ketones with cyclohexene.

2. Results and discussion

Condensation of ferrocenylcarbaldehyde with acetone, acetylacetone and ethyl acetoacetate in benzene or ethanol in the presence of NaOH or piperidine yields *trans*-4-ferrocenyl-3-buten-2-one (**1**), 3-(ferrocenylmethylidene)pentane-2,4-dione (**2a**) and ethyl (*E*)-2-acetyl-3-ferrocenylacrylate (**2b**) which served as our starting material [14,15].

We found that methylketone **1** in presence of 2-PyZnBr (**3a**) or Zn(CH₃)₂ (**3b**) under reflux in benzene did not afford the target

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Diels–Alder adduct (**4**) of 4-ferrocenyl-2-hydroxy-1,3-butadiene (enolization product) with cyclohexene. Instead, two compounds were isolated from the reaction mixture: 4-acetyl-3,5-diferrocenylcyclohexanone (**5**) and 5,8-diferrocenyl-1-hydroxybicyclo-[2.2.2.]octan-3-one (**6**) (Scheme 1).

This encouraging result prompted us to examine the cyclization reactions of *trans*-4-ferrocenyl-3-buten-2-one **1** in other conditions, but positive results were achieved only in benzene (~80–82 °C) with certain cyclohexene, as summarized in Table 1.

Cyclodimers **5** and **6** were isolated by column chromatography on alumina as yellow crystals stable on storage in solid state. The structures of compounds **5** and **6** were established based on the data from IR spectroscopy, ¹H and ¹³C NMR spectroscopy, mass spectrometry, and elemental analysis.

The parameters of the ¹H NMR spectra (number of proton signals, values of chemical shifts and of spin–spin interaction constants) of the aliphatic protons in compounds **5** and **6** confirm the suggested chemical structure of these compounds. Additional information on the structure of compounds **5** and **6** is obtained by the ¹³C NMR spectra. The presence of two signals from quaternary carbon atoms in the ferrocenyl fragments of compounds **5** and **6**, together with the signals from two C₅H₅ groups unambiguously prove the formation of dimers. The absence of CH₃– signals confirms the suggested bicyclic structure of compound **6**. The number of ¹³C NMR signals from the C, CH, CH₂ and CH₃ groups in compounds **5** and **6** correspond to their chemical structure. NMR spectroscopic data suggested that obtained cyclodimers **5** and **6** represented single diastereomeric forms.

The spatial structure of the compound **6** was based on X-ray diffraction analysis of single crystals obtained with crystallization from EtOH/H₂O (4:1). The general view of molecule **6** is shown in Fig. 1. Selected bond lengths and bond angles are given in the legend to this figure. X-ray data show that the structure of cyclodimer **6** is that of 5,8-diferrocenyl-1-hydroxybicyclo-[2.2.2.]octan-3-one, having two fused six-membered carbocycles (bridged bicyclic molecule) with *cis*-orientation of the ferrocenyl substituents. The lengths of the C–C, C–O, and C=O bonds in the carbocyclic fragments and of the C–Fe and C–C bonds in the ferrocenyl substituents, as well as the geometric parameters of the ferrocene sandwiches, are all close to standard values [16].

We found that *trans*-4-ferrocenyl-3-buten-2-one **1** also underwent cyclodimerization and trimerization upon interaction with 1.0 equiv. of ZnXY **2a,b** in the absence of alkenes with formation of two cycloadducts: 4-acetyl-3,5-diferrocenyl-cyclohexanone **5** and 6-acetyl-4,5,7-triferrocenyl-1,9-dehydro-2-decalone (**7**). The best results were obtained when it was refluxed in benzene for 2–3 h, the yield of cyclodimer **5** being ca 45% and cyclotrimer **7** – ca 40% (Scheme 2).

Table 1

Reaction conditions and results of ZnXY-mediated cyclization reactions of *trans*-4-ferrocenyl-3-buten-2-one **1** in benzene in the presence of cyclohexenes (80–82 °C).

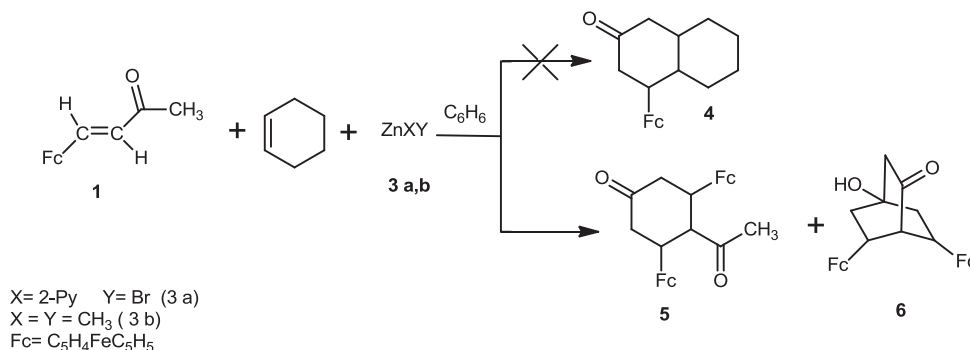
Starting material	Solvent, alkenes	Reaction time (h)	Products	Yield (%)
1 + 2a (2:1)	C ₆ H ₆ , C ₆ H ₁₀	3.0	5 (31)	6 (21)
1 + 2a (1:1)	C ₆ H ₆ , C ₆ H ₁₀	5.5	5 (27)	6 (52)
1 + 2a (1:1)	CH ₂ Cl ₂ , C ₆ H ₁₀	9.0	5 (21)	6 (35)
1 + 2a (1:1)	CH ₂ Cl ₂ , 4-MeC ₆ H ₉	12.0	5 (28)	6 (43)
1 + 2b (2:1)	C ₆ H ₆ , C ₆ H ₁₀	4.0	5 (18)	6 (61)
1 + 2b (2:1)	CH ₂ Cl ₂ , 1-MeC ₆ H ₉	10.0	5 (17)	6 (54)
1 + 2b (1:1)	C ₆ H ₆ , 1-MeC ₆ H ₉	7.0	5 (30)	6 (53)

The compounds **5** and **7** were separated by chromatography and their structures were established from the data of IR, ¹H and ¹³C NMR spectroscopy, mass spectrometry, and elemental analysis. Thus, the ¹H NMR spectra of compound **7** displays one singlet for the one methyl group, three singlets for the three C₅H₅ fragments of the three ferrocenyl substituents, three multiplets for the two CH₂– and five CH– fragments, and one singlet for the one olefinic proton of CH= group. The ¹³C NMR spectra of compound **7**, which also corroborate its structure, displays one signal for carbon atom bearing no hydrogen atoms, two signals for carbonyl carbon atoms, two signals for CH₂ and five signals for CH groups, and three signals for the C_{ipso}Fc carbon atoms of the ferrocene units. The number of signals for the C₅H₄– and Me groups and their chemical shifts correspond completely to structure **7**. According to the ¹H and ¹³C NMR data, cyclotrimer **7** is formed stereospecifically. Despite the presence of four chiral centers in the molecule **7**, this was isolated as single diastereomer.

The transformations of the 3-(ferrocenylmethylidene)pentane-2,4-dione **2a** and ethyl (*E*)-2-acetyl-3-ferrocenylacrylate **2b** with zinc-organic compounds **3a,b** in the presence or absence of alkenes occur analogously (Scheme 3). In all cases, compounds **8a** and **8b** were isolated in good yields (~71–74%).

The structures of compounds **8a** and **8b** were established based on the data from IR, ¹H and ¹³C NMR spectra and X-ray diffraction analysis, which corroborates completely the suggested structures. The ¹H NMR spectra of compounds **8a** and **8b** contained signals for the protons of two ferrocenyl groups, signals for one ABX system for the protons of CH–CH₂ fragments, singlets for aliphatic protons of Fc–CH group. Signals for carbon atoms of two ferrocene units, methyl substituents, carbon atoms bearing no hydrogen atoms, carbon atoms of the carbonyl, methine and methylene groups are all present in the ¹³C NMR spectra.

We obtained final proof that the structures of the cyclodimers **8a** and **8b** are that of 3,5-diferrocenyl-1-hydroxy-2,4,4-triacetylcyclohexene and diethyl 4-acetyl-3,5-diferrocenyl-1-hydroxycyclohexene-2,4-dicarboxylate, respectively, having one six-membered carbocycle each with enolic hydroxy groups in the



Scheme 1.

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