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Friedel–Crafts alkylation of ferrocene with Z-cyclooctene and cyclohexene

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Abstract

Cycloalkylated ferrocene derivatives, potentially useful as liquid burning rate modifiers for the HTPB/AP-based composite rocket propellants, were synthesized by the Friedel–Crafts alkylation of ferrocene with Z-cyclooctene or cyclohexene in the presence of $AlCl_3$ as a Lewis acid catalyst. The reaction with Z-cyclooctene yields a mixture of main products containing up to four C_8H_{15} substituents, each of which exists in several isomeric forms, as recognized by MS and GC–MS techniques. Two isomeric monosubstituted products, cyclooctylferrocene and (1-methylcycloheptyl)ferrocene, isolated by means of preparative GC, were identified by ^{13}C-NMR spectroscopy. In the case of cyclohexene, cyclohexylferrocene and a 2:1 mixture of 1,1′-dicyclohexylferrocene and 1,3-dicyclohexylferrocene were isolated and identified by MS and ^{13}C-NMR spectroscopy. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Ferrocene; Alkylation; Friedel–Crafts; Cyclooctene; Cyclohexene

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1. Introduction

Ferrocenes are known as highly efficient burning-rate catalysts for composite rocket propellants [1,2]. Although ferrocene derivatives are superior to other transition metal compounds for this purpose, their use has some drawbacks arising from their tendency of migration in the bulk of the material and their sensitivity toward oxidation by air [3]. In this way, they are detrimental to the aging behavior and reliability of the propellant. A binuclear ferrocene drivative, 2,2′-bis-(ethylferrocenyl)propane (Catocene) has been developed to reduce the migration tendency [1]. In hydroxyl terminated polybutadiene (HTPB)-based propellants, this additive has a migration rate lower than that of mononuclear ferrocene derivatives such as ethyl- or *n*-butylferrocene. In principle, migration can be completely prevented if the ferrocene is bound to the polymeric binder or is a part of its polyurethane backbone [4]. For this purpose, Butacene (SNPE, France) has been developed, which contains the ferrocene unit chemically bound to the HTPB polymer [1,5]. A large number of polymeric ferrocenes, produced from different precursor monomers, are also found in the literature [4,5]. However, the cost of ferrocene derivatives of this type is quite high due to the laborious syntheses. The high price of Catocene and Butacene, for example, is the main impediment for their use as burning-rate modifier in the rocket applications.

Therefore, the synthesis of new, more easily accessible ferrocene derivatives as effective burning-rate modifiers would be of great importance. Bulky substituents on the cyclopentadienyl rings of ferrocene, such as cyclohexyl or cyclooctyl groups, are anticipated to hinder the migration in the HTPB-based composite propellants without affecting the processing and mechanical properties, the aging behavior and the lifetime of the propellant. Herein we report on the synthesis of cyclohexyl or cyclooctyl substituted ferrocenes by Friedel–Crafts alkylation as potentially useful additives for composite rocket propellants [6,7].

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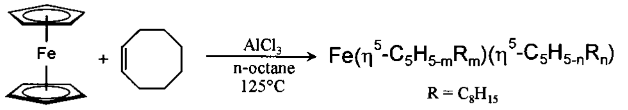
2. Results and discussion

The reaction of ferrocene (**1**) with *Z*-cyclooctene has been explored under various conditions [8]. Among a variety of strong Lewis acids used as catalysts, best results were obtained with anhydrous aluminum chloride. Aluminum chloride has already been shown to catalyze the Friedel–Crafts alkylation of olefins, which involves the carbocation formation by nucleophilic attack of olefin on aluminum [9]. Although in general the reaction was found to be accelerated upon raising the temperature, thermally mild conditions are favorable with respect to minimizing side reactions such as olefin polymerization. Moreover, in the absence of a solvent the reaction has totally failed to yield the desired products, in contrast to the findings of Neuse and Trifan using a related system [9]. Optimum conditions involve heating a 1:4:1 molar ratio of ferrocene (**1**), *Z*-cyclooctene, and aluminum chloride in *n*-octane at 125°C, the lowest temperature at which the system is homogeneous.



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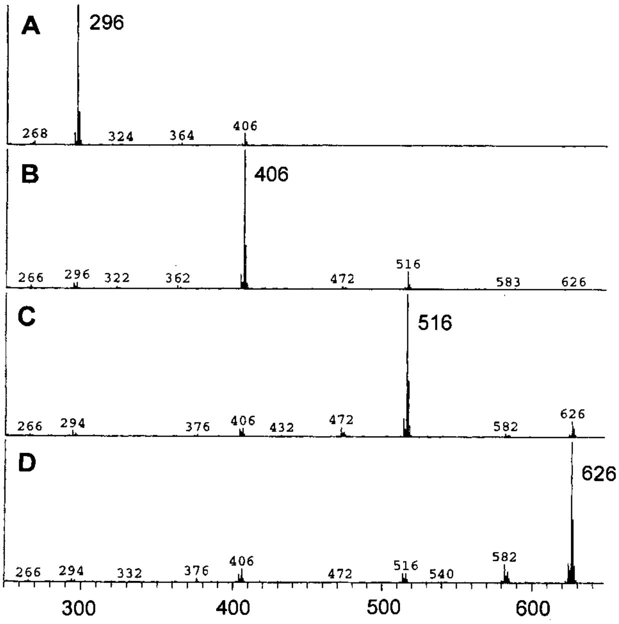
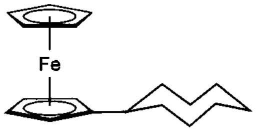


Fig. 1. Mass spectra recorded during the temperature-controlled evaporation of the crude product mixture, $Fe(\eta^5\text{-}C_5H_{5-m}R_m)(\eta^5\text{-}C_5H_{5-n}R_n)$ ($R = C_8H_{15}$), obtained from the Friedel–Crafts alkylation of ferrocene with *Z*-cyclooctene. The selected spectra refer to those temperatures at which the respective molecular ions exhibit maximum intensity: (A) 65°C (M^+ 296, $m+n=1$); (B) 90°C (M^+ 406, $m+n=2$); (C) 150°C (M^+ 516, $m+n=3$); (D) 190°C (M^+ 626, $m+n=4$).

The crude product obtained in this way is a mixture of substituted ferrocenes, $Fe(\eta^5\text{-}C_5H_{5-m}R_m)(\eta^5\text{-}C_5H_{5-n}R_n)$ ($R = C_8H_{15}$), as recognized by means of mass spectrometry with temperature-controlled evaporation of the sample. The series of spectra displayed in Fig. 1 illustrates the successive appearance of ferrocene derivatives with increasing number of C_8H_{15} substituents, each of which exhibits the molecular ion as the most intense peak. Compounds with $(m+n)=1$ (~ 15%), 2 (~ 40%), 3 (~ 35%), and 4 (~ 10%) are the main components of the product mixture, as estimated from the integrated intensities of the respective molecular ions in the spectra recorded throughout the course of the evaporation.

More detailed information is obtained from gas chromatography in combination with MS detection, which reveals the presence of several isomers associated with each of the above molecular ion peaks. Even with only one C_8H_{15} substituent ($M^+ = 296$), three individual species are detected in ca. 10:3:2 ratio. The first two isomers could be isolated by means of preparative GC and, on the basis of their ^{13}C- and $^{13}C\{^1H\}$-NMR spectra, were identified as cyclooctylferrocene (**2**) and (1-methylcycloheptyl)ferrocene (**3**).



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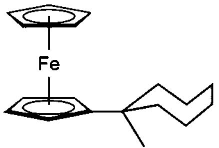

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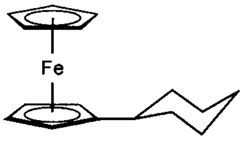
In either case, the cyclopentadienyl carbon atoms give rise to four signals, one singlet associated with the carbon atom carrying a substituent, two doublets for the remaining two pairs of carbon atoms in the substituted ring, and one doublet of higher intensity for the unsubstituted ring. Consistent with the pattern expected for the cyclooctyl substituent, the main product (**2**) exhibits five signals in the aliphatic region, one of which is a doublet, while the other four appear as triplets (seven CH_2, six of which are pairwise equivalent).

The same number of five aliphatic carbon resonances is also found in the spectrum of compound **3**. However, in this case one singlet and one quartet are observed in addition to three triplets of comparable intensities (six CH_2, pairwise equivalent) indicative of cyclooctyl ring contraction with formation of the 1-methylcycloheptyl group. The ring contraction leading to the compound **3** might be attributed to the formation of a more stable carbocation during the course of reaction, which, in fact, requires further investigation. The identity of the third isomer with $M^+ = 296$ remains a matter of speculation. Further ring contraction of the C_8H_{15} substituent with conversion into an ethyl- or dimethyl-cyclohexyl group seems possible [10].

Due to the thermal decomposition under the conditions of preparative gas chromatography, none of the numerous polyalkylated ferrocenes with $M^+ = 406$ ($m+n=2$), 516 ($m+n=3$), and 626 ($m+n=4$), recognized by means of GC–MS combination, could be isolated from the reaction mixture. Thus, no information concerning the occurrence of homoannular versus heteroannular multiple substitution is available from this system.

Fortunately, the analogous Friedel–Crafts alkylation of ferrocene with cyclohexene gives a clue in this respect. GC analysis of the crude product shows two prominent peaks, each accounting for about one third of the material. These two components, separated from the reaction mixture by means of preparative gas chromatography with 98 and 89% purity (by GC analysis), are recognized as mono- and dialkylated ferrocenes on the basis of the molecular ions, $M^+ = 268$ and 350, respectively, observed in the mass spectra of the two samples. In addition, the GC of the crude reaction mixture shows some unreacted ferrocene (less than 10%) and a group of peaks (altogether less than 10%) which, considering the retention time, are attributable to trialkylated ferrocenes.



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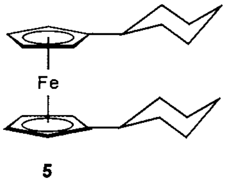
The first one of the two isolated samples proved to be pure cyclohexylferrocene (**4**), as concluded from the ^{13}C- and $^{13}C\{^1H\}$-NMR spectra. In addition to a total number of four signals associated with the carbon atoms of the unsubstituted and the monosubstituted cyclopentadienyl rings, one doublet and three triplets are observed in the aliphatic region, indicative of the CH and CH_2 units of a cyclohexyl substituent. The compound **4** has been obtained from the catalytic hydrogenation of phenylferrocene [11] or cyclohexenylferrocene [12], and characterized on the basis of ^{1}H-NMR chemical shifts that are in agreement with our data, though obviously not enough for a thorough structural assignment.

The second sample contains two products in ca. 2:1 ratio, as recognized from a more careful analysis by gas chromatography. Accordingly, the ^{13}C- and $^{13}C\{^1H\}$-NMR spectra exhibit two sets of resonances with relative intensities that are consistent with the above ratio of the two components and, altogether, identify the more abundant compound as 1,1′-dicyclohexylferrocene (**5**) and the other one as 1,3-dicyclohexylferrocene (**6**).



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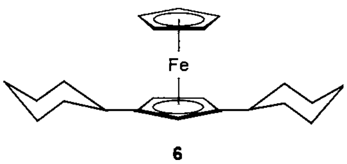

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The signal pattern associated with **5** clearly reflects the presence of two equivalent, monosubstituted cyclopentadienyl rings. It exhibits three signals for the cyclopentadienyl carbons, viz., two doublets for the two CH pairs and one singlet for the unsubstituted carbon in each ring. Four resonances are observed in the aliphatic region: one doublet for the CH carbon and three triplets for the single CH_2 group and the two CH_2 pairs.

With this assignment, a total of four C_p carbon signals is left over for the second component of the sample, consistent with a homoannularly disubstituted ferrocene. In detail, this part of the spectrum includes, in addition to one intense doublet for an unsubstituted C_p ligand, one singlet and two more doublets, attributable to either a 1,2- or 1,3-disubstituted C_p ring. The distinction between these two possibilities, in favor of structure **6**, rests on the relative intensities and positions of the latter two doublets, one of which represents two equivalent CH carbons and, thus, is of higher intensity than the other one. The weaker signal appears at higher field and, hence, the corresponding CH unit is concluded to be located between the two substituted carbon atoms, as indicated in formula **6**. In the aliphatic region, compound **6** exhibits five signals, i.e. one more than **5**. This is due to the fact that the cyclohexyl rings of **6**, unlike those of **5**, lack an internal plane of symmetry. Hence, all six carbon atoms are chemically different, but accidental overlap of two CH_2 resonances reduces the number of resonances to five (a doublet for one CH and four triplets for the five CH_2).

1,1′-Dicyclohexylferrocene (**5**) has already been obtained from the reaction of cyclopentadienylidenecyclohexane with lithium aluminum hydride or potassium hydroxide followed by iron(II) chloride and characterized on the basis of sole elemental analysis [13]. The alkylation of ferrocene with cyclohexene in the presence of boron trifluoride as a Lewis acid catalyst has been reported to give also the compound **5**, in addition to cyclohexylferrocene **4**, both characterized on the basis of elemental analysis and IR spectral data [14].

As previously reported for many other olefins [8], multiple substitution occurs to a large extent in the Friedel–Crafts alkylation of ferrocene with either cyclooctene or cyclohexene. Disubstitution takes place preferentially in the heteroannular fashion, as explicitly proven for the case of cyclohexene, probably because of the steric effect of the bulky cycloalkyl groups [8].

The effect of the $Fe(\eta^5\text{-}C_5H_{5-m}R_m)(\eta^5\text{-}C_5H_{5-n}R_n)$ product mixtures, with both R = cyclooctyl and cyclohexyl, on the thermal decomposition of ammonium perchlorate and their performance as burning rate modifier in the HTPB/AP-based composite rocket propellants are currently under investigation. The results of these studies will be reported elsewhere.

3. Experimental

3.1. General

Ferrocene (Merck), cyclohexene, *Z*-cyclooctene, and aluminum chloride (Aldrich) were used as received, while *n*-octane (Aldrich) was distilled from sodium–benzophenone ketyl prior to use. All reactions were performed under nitrogen atmosphere. NMR spectra were recorded on a Bruker AM 400 instrument (400.1 MHz for ^{1}H and 100.6 MHz for ^{13}C).

3.2. Friedel–Crafts alkylation of ferrocene with *Z*-cyclooctene

A solution of ferrocene (**1**) (10.00 g, 0.054 mol), *Z*-cyclooctene (28 cm^3, 0.20 mol), and anhydrous aluminum chloride (7.20 g, 0.054 mol) in *n*-octane (50 cm^3) was refluxed (125°C) for a period of 8 h. The gradual disappearance of ferrocene was followed by TLC, using 2:1 methanol–dichloromethane as eluent. After cooling down, the mixture was quenched with ice-water and then extracted with methylene chloride (4 × 150 cm^3). The combined extracts were dried over anhydrous sodium sulfate and then filtered through a layer of celite and silica gel. Removal of the volatiles in vacuo yielded a brown viscous oil (17.20 g).—By means of MS analysis (Finnigan MAT 8200 instrument, EI ionization), with temperature-controlled evaporation of the sample (-20°C to $+380$°C), the crude product mixture was shown to contain about 15% mono-, 40% di-, 35% tri-, and 10% tetrasubstituted ferrocenes (M^+ = 296, 406, 516, and 626, respectively; representative spectra are displayed in Fig. 1). GC (HP 5890/2 instrument; capillary column with 0.5 μm OV1 film, Ø = 0.25 mm and l = 10 m; 1.2 bar H_2 carrier gas; temperature 70–300°C, 10°C min^{-1}) in combination with MS detection (Finnigan MAT SSQ7000, EI ionization) revealed the presence of several isomers associated with each molecular ion.—Preparative GC (Gerstel AMPG-60 apparatus; packed column with Silicone SE-30 on 60–80 mesh Chromosorb P, Ø = 20 mm and l = 1.5 m; N_2 carrier gas, 565 cm^3 min^{-1}; 350°C and 230°C injection and column temperature, respectively; 0.5 cm^3 of a sample solution in toluene injected per cycle, with back flushing of higher boiling components in each cycle) was employed to separate cyclooctylferrocene (**2**) (91% purity by GC) and (1-methylcycloheptyl)ferrocene (**3**) (84% purity by GC; 95% in a second run with pre-enrichment from of the crude product by means of HPLC on Nucleosil® N-7-C18 with methanol as the mobile phase).

NMR data of **2** ($CDCl_3$). ^{13}C: δ 98.01 (s; 1 C at C_p), 68.43 (d, ~170 Hz; 5 CH at C_p), 66.86 (d, ~ 170 Hz; 2 CH at C_p), 66.65 (d, ~ 170 Hz; 2 CH at C_p), 37.40 (d, 126 Hz; 1 CH), 34.07 (t, 124 Hz; 2 CH_2), 27.11 (t, 124 Hz; 2 CH_2), 26.36 (t, 127 Hz; 1 CH_2), 25.89 (t, 124 Hz; 2 CH_2). ^{1}H: δ 4.12 (s, 5 H), 4.05 (broad s, 4 H), 2.49 (m, 1 H), 1.92 (m, 2 H), 1.74–1.42 (m, 14 H). MS: 296 (M^+, 100), 234 (13), 212 (18), 199 (8), 186 (9), 121 (15), 56 (7).

NMR data of **3** ($CDCl_3$). ^{13}C: δ 103.25 (s; 1 C at C_p), 68.12 (d, 174 Hz; 5 CH at C_p), 66.82 (d, J_{CH} = 175 Hz; 2 CH at C_p), 65.19 (d, 169 Hz; 2 CH at C_p), 42.31 (t, 126 Hz; 2 CH_2), 36.12 (s; 1 C), 30.80 (t, 126 Hz; 2 CH_2), 28.75 (q, 125 Hz; 1 CH_3), 23.53 (t, 124 Hz; 2 CH_2). ^{1}H: δ 4.03 (s, 5 H), 3.96 (m, 4 H), 1.57 (m, 2 H), 1.50–1.30 (m, 10 H), 1.11 (s, 3 H). MS: 296 (M^+, 100), 239 (15), 226 (11), 199 (8), 186 (19), 121 (13), 56 (7).

3.3. Friedel–Crafts alkylation of ferrocene with cyclohexene

A solution of ferrocene (**1**) (10.00 g, 0.054 mol), cyclohexene (28 cm^3, 0.20 mol), and anhydrous aluminum chloride (7.20 g, 0.054 mol) in *n*-octane (50 cm^3) was reacted under similar conditions as described above, yielding 16.0 g crude product as a brown viscous oil.—GC analysis (Siechromat instrument; capillary column with 0.5 μm OV1 film, Ø = 0.25 mm and l = 10 m; 1.2 bar H_2 carrier gas; temperature 70–280°C, 8°C min^{-1}, FID) of the crude product shows, apart from some unreacted ferrocene, two major product peaks (each accounting for about one third of the material) and an additional group of product peaks (less than 10%) at longer retention time.—Preparative GC (similar conditions as described above) was employed to separate cyclohexylferrocene (**4**) (first main fraction, 98% purity by GC) and a mixture of 1,1′-dicyclohexylferrocene (**5**) and 1,3-dicyclohexylferrocene (**6**) (second main fraction, 58% of **5** and 32% of **6**, by GC) from the crude product.

NMR data of **4** ($CDCl_3$). ^{13}C: δ 95.94 (s; 1 C at C_p), 68.32 (d, 175 Hz; 5 CH at C_p), 66.72 (d, 175 Hz; 2 CH at C_p), 66.09 (d, 173 Hz; 2 CH at C_p), 37.55 (d, 126 Hz; 1 CH), 34.44 (t, 127 Hz; 2 CH_2), 26.73 (t, 125 Hz; 2 CH_2), 26.45 (t, 125 Hz; 1 CH_2). ^{1}H: δ 4.12 (s, 5 H), 4.06 (s, 4 H), 2.25 (m, 1 H), 1.98 (m, 2 H), 1.76 (m, 2 H), 1.45–1.10 (m, 6 H). MS: 268 (M^+, 100), 225 (9), 199 (13), 198 (14), 186 (10), 134 (8), 121 (22), 56 (12).

^{13}C-NMR data of **5** and **6** ($CDCl_3$). **5**: δ 95.95 (s; 2 C at C_p), 67.61 (d, 174 Hz; 4 CH at C_p), 66.60 (d, 172 Hz; 4 CH at C_p), 37.54 (d, ~127 Hz; 2 CH), 34.52 (t, 127 Hz; 4 CH_2), 26.75 (t, ~127 Hz; 4 CH_2), 26.45 (t, ~127 Hz; 2 CH_2). **6**: δ 94.79 (s; 2 C at C_p), 68.98 (d, 175 Hz; 5 CH at C_p), 64.70 (d, ~174 Hz; 2 CH at C_p), 64.59 (d, ~174 Hz; 1 CH at C_p), 37.60 (d, ~127 Hz; 2 CH), 34.37 (t, ~127 Hz; 2 CH_2), 34.24 (t, ~127 Hz; 2 CH_2), 26.73 (t, ~127 Hz; 4 CH_2), 26.50 (t, ~127 Hz; 2 CH_2). MS of **5**/**6**: 350 (M^+, 100), 268 (4), 266 (4), 200 (4), 199 (5), 198 (6), 186 (5), 134 (5), 121 (6), 56 (4).

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