

DIELS-ALDER REACTION OF ACRYLOYLFERROCENE WITH 1-PHENYL-1,3-BUTADIENE CATALYSED BY HOMOIONIC FORMS OF MONTMORILLONITE

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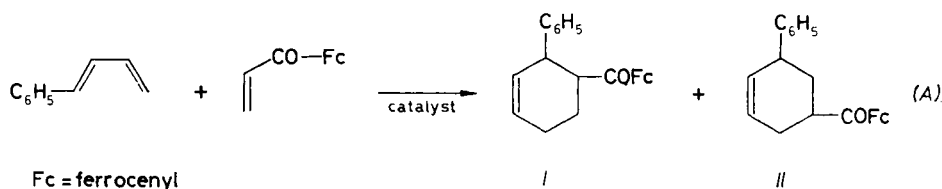
Diels-Alder addition of acryloylferrocene to 1-phenyl-1,3-butadiene catalysed by homoionic forms of montmorillonite proceeds with higher selectivity and yields than does the reaction catalysed with aluminium trichloride. The catalytic activity of M^{n+} -montmorillonites decreases in the sequence: Al^{3+} , Cr^{3+} , Co^{2+} , Fe^{3+} , and Cu^{2+} .

Recently, considerable attention has been paid to organic reactions on inorganic supports¹⁻³, including bentonite or montmorillonite which is the basic part of the former material. Laszlo^{4,5} studied dimerization of conjugated dienes and addition of methyl vinyl ketone to cyclopentadiene catalysed with some homoionic forms of montmorillonite. The author found that the reactions proceed fast and with high endo-exo selectivity. The reaction of cyclopentadiene with methyl vinyl ketone was catalysed by $K10-Fe^{3+}$ montmorillonite⁵ (the trade mark for H^+ -montmorillonite-K10-montmorillonite), using 4-tert.butylphenol as co-catalyst. The exo to endo isomers ratio varied from 1 : 9 to 1 : 19, depending on the solvent used. The best results were achieved with the use of dichloromethane as the solvent. In our previous works^{6,7} we discovered that the oxidative coupling of anisole to give 1,4-dimethoxybiphenyl as well as ferrocenylmethylation of C acids gives similar results, irrespective of whether the reactions are catalysed by montmorillonite or bentonite.

In the present work we examined the possibility to catalyze Diels-Alder reaction of less reactive substrates by different homoionic forms of montmorillonite or of bentonite. The use of acryloylferrocene and 1-phenyl-1,3-butadiene enabled us to investigate also the effect of catalysts on the relative proportion of the head to head with respect to head to tail products. Furthermore, due to its colourness, the ferrocenyl derivative allowed to follow easily the reaction course (TLC) and simplified also chromatographic separation. The results presented in Experimental and in the following table which summarizes the yields of 3-phenyl-4-ferrocenoylcyclohexene achieved with different catalysts show that homoionic forms of montmorillonite and of bentonite (the results in parentheses) — except for Cu^{2+} -montmorillonite are better catalysts than is aluminium trichloride:

| M^{n+} | | | | | | | | |
|---------------------------------|----------------|-----------|---------------|---------------|---------------|---------------|----------|---|
| montmorillonite -(bentonite) | KIO- Fe^{3+} | Fe^{3+} | (Al^{3+}) | (Cr^{3+}) | (Cu^{2+}) | (Co^{2+}) | $AlCl_3$ | 0 |
| Yield(%) | 67 | 67 | 100 | 95 | 54 | 81 | 66 | 0 |

The advantages of these catalysts are not only the higher yields and simple treatment of the reaction mixture but also high selectivity of the addition which yields predominantly one of two possible isomers *I*, *II*, i.e. 3-phenyl-4-ferrocenoylcyclohexene (*I*). The structure of this product was confirmed by its 1H NMR spectrum measured



with Bruker AM 300 (300 MHz) spectrometer. The spectrum shows two multiplets of aromatic protons at δ 7.30 (3 H) and 7.15 (2 H). Signals of ethylenic protons in positions 1 and 2 lie at δ 6.16 and 5.94 and are multiplets. Signals at δ 4.97 (2 H), 4.67 (2 H) and 4.27 (5 H) correspond to ferrocene protons and these at δ 4.07 and 3.65 to protons in positions 3 and 4. Signals of methylenic protons with δ 2.43 (2 H), 2.13 (1 H), and 1.94 (1 H) are multiplets. In addition to the above assignment, the compound structure was further evidenced by decoupling experiments. The selective decoupling of the δ 2.43 signal has simplified the original multiplet with δ 6.16 to doublet having interaction constant $J = 9.7$ Hz and the signal with δ 5.94 to doublet-doublet with $J = 9.7$ and 4.5 Hz, respectively. The signals of protons in positions 3 and 4 remained unchanged, which confirms the structure of 3-phenyl-4-ferrocenoylcyclohexene. Further evidence was obtained by selective decoupling of other signals corresponding to protons in positions 1, 2, 3, and 4.

Attempted Diels-Alder reaction of 1-phenyl-1,3-butadiene with cinnamoylferrocene, using montmorillonite as the catalyst, has not been successful. However, the reaction does not proceed also with aluminium trichloride. The reason of this failure is undoubtedly the low reactivity of cinnamoylferrocene.

EXPERIMENTAL

Melting points were determined with Kofler hot plate and were not corrected. 1H NMR spectra of C^2HCl_2 (99% of 2H isotope) solutions of the compounds were recorded with Tesla BS 487 (80 MHz) and Bruker AM 300 (300 MHz) spectrometers, using tetramethylsilane as internal

reference. Chemical shifts are expressed in δ units. Chromatography was made with the use of Silikagel L 100/250 (Lachema Brno). Bentonite containing 80% of montmorillonite was obtained as filtration cake from Rudné bane Banská Bystrica (locality Jelšovský Potok)⁶. Starting compounds were prepared by reported procedures as indicated: acryloylferrocene⁸, 1-phenyl-1,3-butadiene⁹ and 4-tert.butylphenol¹⁰, KIO-Fe³⁺ montmorillonite¹¹.

Isolation of Natural Montmorillonite (Ca²⁺, Mg²⁺)

Bentonite (760 g, dried at 105–110°C for 24 h) was thoroughly stirred in 38 dm³ of distilled water and then allowed to settle down. A total of 20 dm³ of the suspension (the upper layer) was placed in another vessel, then 100 ml of calcium chloride solution (1 mol dm⁻³ conc.) were added. After settling down, the montmorillonite was filtered off and dried at 105–110°C for 24 h.

Synthesis of Mⁿ⁺-montmorillonites (Mⁿ⁺ = Ca²⁺, Cu²⁺, Co²⁺, Fe³⁺, and Cr³⁺)

Natural montmorillonite (10 g) was added to 50 ml of 0.1M solution of the appropriate metal salt (CaCl₂, CuCl₂, Co(NO₃)₂, and CrCl₃). Suspension of the salt was thoroughly shaken for 2 h and then allowed to settle down for 24 h. The solution was decanted and added again to 50 ml of the salt solution. This procedure was repeated six times. Mⁿ⁺-montmorillonite was filtered off and washed with water until free ions were removed. Then, the catalyst was washed with 20 ml of 50% ethanol and dried at 105–110°C for 24 h. The same procedure was used to prepare Mⁿ⁺-bentonites. The content of exchangeable ions was determined after their release with phenylammonium chloride, using usual analytical methods. A total of 50 ml of phenylammonium chloride solution were used *per* 1 g of the montmorillonite.

Synthesis of H⁺-montmorillonite

Natural montmorillonite (10 g) was added to 5% hydrochloric acid and the suspension was heated to 60°C for 2 h. After 24 h-sedimentation, the mixture was decanted, the residue was filtered off and washed with distilled water until negative test on the presence of chloride ions. After washing with 5% ethanol, H⁺-montmorillonite was dried at 105°C.

Reaction of Acryloylferrocene with 1-Phenyl-1,3-butadiene

Catalysed with Mⁿ⁺-montmorillonites

1-Phenyl-1,3-butadiene (0.13 g, 1 mmol), 0.06 g (0.4 mmol) of 4-tert.butylphenol, and 0.65 g of Mⁿ⁺-montmorillonite were added successively to a solution of 0.24 g (1 mmol) of acryloylferrocene in 20 ml of dichloromethane. The mixture was then stirred at 25°C for 24 h. The catalyst was filtered off and washed thoroughly with dichloromethane. After solvent removal by distillation under reduced pressure, the residue was chromatographed on silica gel (cyclohexane-ethyl acetate 9 : 1). First, trace amounts of two unidentified compounds were obtained. The third band contained 3-phenyl-4-ferrocenoylcyclohexene, m.p. 138–140°C (benzene-petroleum ether). The yields are presented in the already mentioned table. For C₂₃H₂₂FeO (370.7) calculated: 74.6% C, 5.98% H, 15.08% Fe; found: 74.86% C, 6.13% H, 15.05% Fe. ¹H NMR spectrum: 7.2–7.0 (5 H, m, C₆H₅), 6.0–5.7 (2 H, m, CH=CH), 4.8 (2 H, t, H_a), 4.5 (2 H, t, H_b), 4.1 (5 H, s, C₅H₅), 3.9 (1 H, m, CHCO), 3.48 (1 H, m, C₆H₅CH), 2.25 (2 H, m, CH₂), 1.90 (2 H, m, CH₂).

Reaction of Acryloylferrocene with 1-Phenyl-1,3-butadiene

Catalysed by Aluminium Trichloride

To solution of 0.2 g (0.8 mmol) of acryloylferrocene in 20 ml of dichloromethane, 0.1 g (0.8 mmol)

of 1-phenyl-1,3-butadiene and 0.1 g of aluminium trichloride were added. The mixture was stirred at 25°C for 24 h, acidified with hydrochloric acid and then poured into water. After reduction of ferricinium salts with sodium hydrogen sulphite, the organic material was extracted with dichloromethane. The dichloromethane solution was washed thoroughly with saturated sodium hydrogen carbonate solution and then with water. After drying (Na_2SO_4), dichloromethane was distilled off under reduced pressure and the residue was chromatographed on silica gel column. The first band gave 0.05 g of unidentified yellow oil, the second afforded 0.05 g (16%) of a compound melting at 60–63°C (benzene–petroleum ether) — most likely 3-phenyl-5-ferrocenoylcyclohexene (*II*) — and finally 0.2 g (66%) of 3-phenyl-4-ferrocenoylcyclohexene, m.p. 138–140°C.

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