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Stereoselective Synthesis and Diels-Alder Reactions of bis-Ether 1,3 Dienes. A further Test for Cooperativity during Cycloaddition Reactions.

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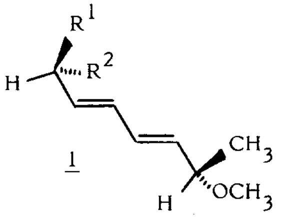
Summary : A stereoselective synthesis of dienes 1a and 1b, using butadiene-iron tricarbonyl complexes, is described. Higher diastereoselectivity is observed during Diels-Alder reaction of 1a as compared with 1c, affording good evidence for cooperativity in these cycloadditions.

A "Principle of cooperativity in asymmetric induction" was proposed recently by Tolbert and Ali (1). Results obtained with bornyl type fumarate esters are in good agreement with this theory, although relatively small differences in diastereomer ratios are obtained. It then seemed interesting to us to check this cooperativity with other models which would be also more suitable for theoretical calculations.

The purpose of this letter is :

1) To show that functionnalized butadiene iron tricarbonyl complexes (2) allow a stereoselective synthesis of dienes 1a and 1b of known relative configuration.



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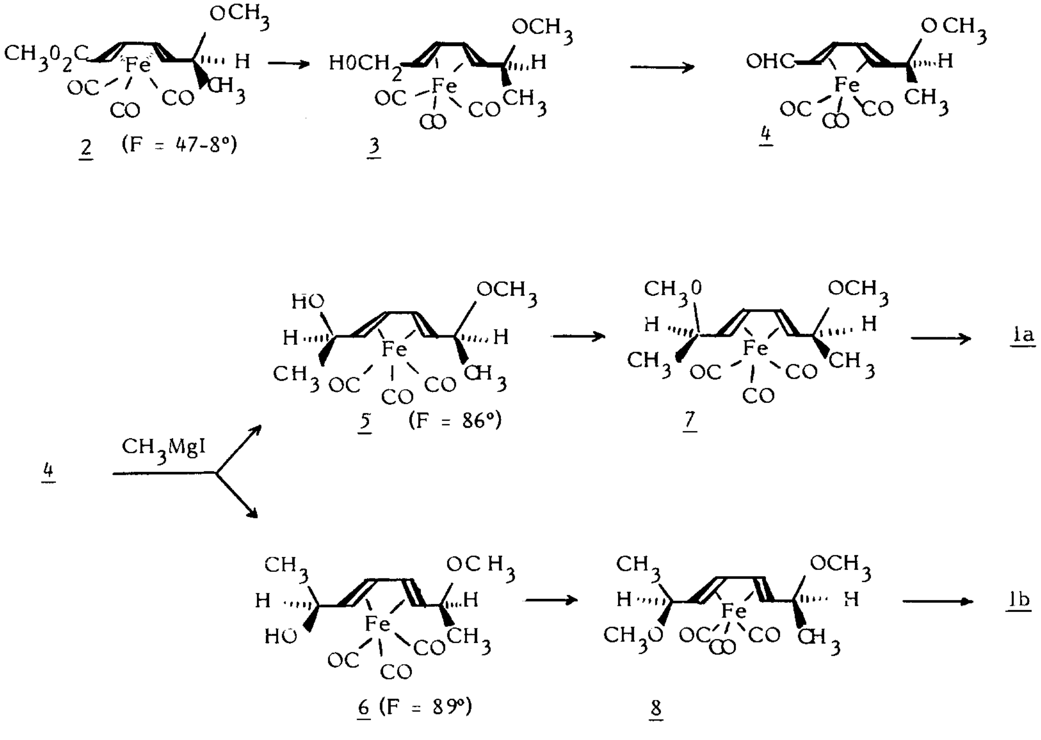
a : R^1 = CH$_3$, R^2 = OCH$_3$
b : R^1 = OCH$_3$, R^2 = CH$_3$
c : R^1 = R^2 = H

2) To describe Diels-Alder reactions of these dienes with TCNE. The higher diastereoselectivity observed in the case of 1a as compared with monoether 1c, chosen as a model, proves that cooperativity operates. Furthermore, our results reveal the orientation of the directive effect exerted by a methyl ether function during cycloadditions, a subject of much recent interest (3).

I - Synthesis of the dienes

Complex 2 (racemic) (4), obtained as described in the preceding paper, is reduced (Dibal, ether, -15°, 90 %) to 3. Oxidation to 4, without decomplexation was best accomplished using Landensberg's method (5) (SO_3-Py, Et_3N, DMSO, 65 %).

Scheme 1

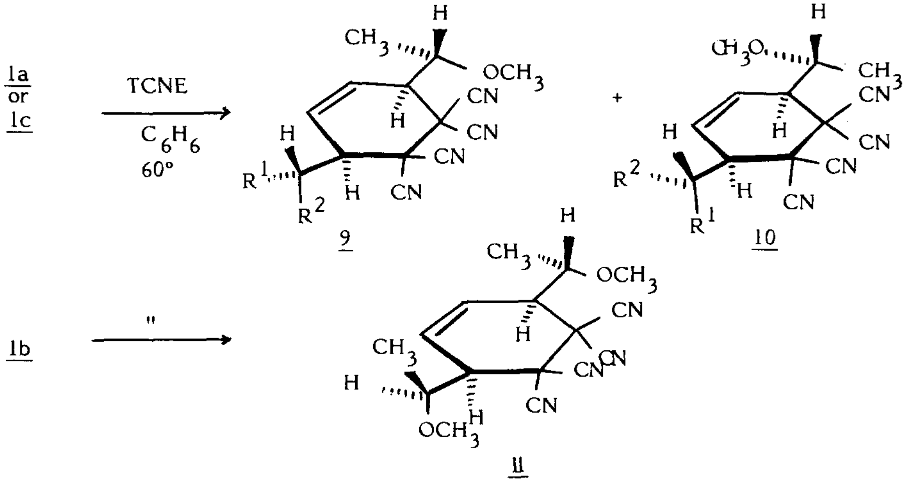


Reaction with CH_3MgI leads to a 54/46 mixture of 5 and 6 (overall yield 52 %) easily separated by chromatography (6). Protection ($HC(OMe)_3$, H^+, 80 %) gives 7 and 8. NMR data for these complexes establishes unambiguously their stereochemistry : due to its symmetry 7 has only six signals in the ^{13}C NMR spectrum when 8 has the expected 11 line spectrum (7) ; similar conclusion may be deduced from ^{1}H NMR (7). Decomplexation (Me_3NO, $2H_2O$; 4Å Mol. Sieves, CH_2Cl_2, 40 %) gives respectively 1a and 1b (8).

II - Diels Alder Reactions

Our results are summarized in scheme 2. Reaction of the model diene 1c [(9)] with TCNE (C_6H_6, 60°, 12 h) gives quantitatively, under kinetic control, a 2/1 (NMR, GC) mixture of 9c (F = 156°) and 10c (F = 131°) separated by fractionnal crystallisation (CH_2Cl_2). The structure of 9c was established by x-ray analysis [(10)]. Under the same conditions, reaction of 1a gives a 85/15 (NMR, GC) mixture of adducts 9a and 10a. The major adduct 9a (F = 164°) was isolated (fractionnal crystallisation, CH_2Cl_2) and submitted to x-ray analysis [(10)]. As expected, isomer 1b gives a single adduct 11 different (^1H, ^{13}C NMR) from compounds 9a and 10a.

Scheme 2



These results deserve three main comments :

- The large change in diastereoisomeric ratio (from 2 to 5.7) is in excellent agreement with the cooperativity principle [(1)].

- As discussed by Houk [(11)] the stereoselectivity of these cycloadditions can be interpreted in terms of Felkin-Ahn's model [(12)], methyl behaving here as the "largest" group. Theoretical studies regarding this problem are under way in our laboratory.

- Due to the ready access to chiral monoalcohol and ether derivatives (preceding paper) it clearly opens a route to dienes bearing two asymmetric allylic carbon atoms with control of their absolute configuration.

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(4) Reactions were performed with racemic complexes ; For convenience only one enantiomer is shown on the scheme. Similar reactions have been carried out starting with diastereoisomer of 2 (compound 5 in preceding paper) : they also gave 1a and 1b.

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(6) SiO_2, ether + light boiling petroleum ether 1/1 : 5 : Rf = 0,21, 6 : Rf = 0,53.

(7) 7 : ^{13}C NMR (C_6D_6) δ : 212,3 ; 83,3 ; 78,8 ; 65,7 ; 55,6 ; 22,4 ; ^{1}H NMR ($CDCl_3$) δ : 1,30 (CH_3-CH).
8 : ^{13}C NMR (C_6D_6) δ : 212,5 ; 82,8 ; 81,3 ; 79,1 ; 77,1 ; 69,3 ; 64,6 ; 55,9 ; 55,6 ; 22,6 ; 21,7. ^{1}H NMR ($CDCl_3$) : 1,24 and 1,32 (CH_3-CH).

(8) Unlike their organometallic precursors, 1a and 1b have identical ^{1}H (80 MHz) and ^{13}C (23,15 MHz) NMR spectra.

(9) Prepared from hexadienal in two steps (CH_3MgI ; NaH + CH_3I ; 52 % overall yield).

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