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STEREO- AND ENANTIOSELECTIVE SYNTHESIS OF SOME E,Z DIENOLS AND ETHERS.

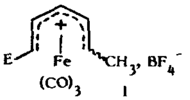
René GRÉE, Mohammed LAABASSI, Paul MOSSET and Robert CARRIÉ *

Groupe de Recherches de Physicochimie Structurale, U.A. C.N.R.S. n° 704,
Université de Rennes I, 35042 RENNES CEDEX, FRANCE.

Summary : Functionnalized E,Z dienes (-) 2 have been prepared in a highly stereo- and enantioselective manner using chiral pentadienyl iron tricarbonyl complexes 1.

Although useful intermediates in organic synthesis, dienes bearing chiral carbon atoms in allylic position are not always easily prepared. We proposed recently a new method for the synthesis of functionnalized E,E dienols and corresponding ethers (1). Both for synthetic and mechanistic purposes, we needed the same derivatives but with a different stereochemistry of the double bonds. The purpose of this letter is to show that type 1 cations are easily accessible in optically active form. They furthermore allow an highly stereo-and enantioselective synthesis of functionnalized E,Z dienols and corresponding ethers (-) 2.

E = CO_2CH_3



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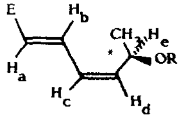
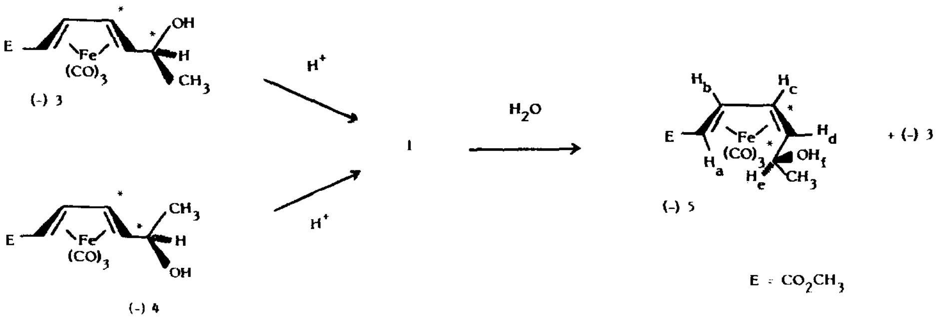


(-) 2

a : R = H
b : R = CH_3

The reaction of the easily prepared alcohol (-) 3 (1) under strong acid conditions[HBF_4 in $(EtCO)_2O$ then Et_2O] gives a crystalline cation 1. Hydrolysis of freshly prepared 1 gives a 95/5 mixture of the E,Z complex (-) 5 and (-) 3 (60 % overall yield from 3). They are separated by chro-



E = CO_2CH_3

matography and structure of (-) **5** is established using spectroscopic data (2). Only one diastereoisomer of (-) **5** is obtained and 5 S configuration is attributed by analogy with Maglio and Palumbo's work (3). Decomplexation of (-) **5** is best accomplished using $Ce(NH_4)_2(NO_3)_6$ in isopropanol-water (10/1) at -15° giving (-) **2a** (oil, 80 % yield) contaminated by 5 % (^1H and ^{13}C NMR) of the corresponding E,E isomer. NMR data of **2** establishes the E,Z stereochemistry (4). Optical purity (e.e. > 90 %) is checked by NMR using Eu $(tfc)_3$ complexes. Alkylation of (-) **2a** by Me_2SO_4 (5) gives ether (-) **2b** (oil, 75 % yield) (6).

Although in lower yields, the diastereoisomeric complex (-) **4** *give identical results : the same* alcohols (-) **5** and then (-) **2** (in 40% overall yield from **4**)are obtained. It is thus not necessary to separate these compounds before preparing cations **1** (7).

The overall transformation (-) **3** → (-) **5** appears as an interesting original process ; one has to notice however the strong influence of the ester group since hydrolysis of similar cations, but bearing only methyl groups give selectively E,E complexed alcohols (8).

Further use of both these chiral cations and the E,Z dienols are currently under investigation in our laboratory.

References and notes

(1) R. GRÉE, M. LAABASSI, P. MOSSET and R. CARRIÉ, Tetrahedron Lett., 25, 3693 (1984).

(2) (-) **5** :$[\alpha]_D^{25}$ = -166° (MeOH), c = 0.12) ; IR (film ; ν_{cm}-1) : 3400 (broad, OH) ; 2052, 1980 (C≡O), 1709 (C=O). RMN ^1H (80 MHz,$CDCl_3$, δ) ; 6,10 (d.d.d ; J_{ab} = 8.5 ; J_{bc} = 5.3 ; J_{bd} = 1.1 ; H_b) ; 5.26 (d.d.d; J_{cd} = 7.7 ; J_{ac} = 0.9 ; H_c) ; 3.69 (s ; 3H ; $CO_2C\underline{H}_3$) ; 3.37 (d.q ; J_{de} = 8.5 ; H_e) ; 3.30 (broad ; H_f) ; 2.75 (d.d.d ; H_d) ; 2.15 (d.d ; H_a) ; 1.36 (d ; J = 5.8 ; $C\underline{H}_3$).

(3) G. MAGLIO and R. PALUMBO ; J. Organomet. chem., 76, 367 (1974) and ref. therein.

(4) (-) **2a** : $[\alpha]_D^{25}$ = -85° (MeOH, c = 0.19) ; IR (film ; ν_{cm}-1) : 3400 (broad, OH) ; 1715 (C=0) ; 1636, 1605 (C=C). RMN ^1H (80 MHz, $CDCl_3$, δ) ; 7.61 (d.d ; J_{ab} = 15.2 ; J_{bc} = 10,6 ; H_b) ; 6.11 (d.d ; J_{cd} = 10.8 ; H_c) ; 5.90 (d ; H_a) ; 5.83 (d.d ; J_{de} = 7.8 ; H_d) ; 4.90 (d.q ; H_e) ; 3.77 (s, 3H) ; $CO_2C\underline{H}_3$); 3.16 (broad ; H_f) ; 1.33 (d ; J = 6.2 ; $C\underline{H}_3$).

(5) Procedure similar to that described in reference 1.

(6) (-) **2b** : $[\alpha]_D^{25}$ = -56° (MeOH), c = 0.13) ; IR (film, cm^{-1},ν) : 1718 (C=0) ; 1641, 1637, 1604 (C=C). RMN (80 MHz ; $CDCl_3$, δ) : 7.60 (d.d.d ; J_{ab} = 15.2 ; J_{bc} = 11.4 ; J_{bd} = 0.8 ; H_b) ; 6.24 (d.d.d.d. ; J_{ac} = 0.5 ; J_{cd} = 10.9 ; J_{ce} = 0.8 ; H_c) ; 5.93 (d.d.d ; J_{ad} = 0.6 ; H_a) ; 5.71 (d.d.d.d ; J_{de} = 8.6 ; H_d) ; 4.36 (d.q ; H_e) ; 3.77 (s, 3H, $CO_2C\underline{H}_3$) ; 3.28 (s, 3H, $OC\underline{H}_3$) ; 1.27 (d ; J = 6.3 ; $C\underline{H}_3$).

(7) Although giving the same alcohols by hydrolysis, cations **1** obtained from (-) **3** or (-) **4** are not identical : other reagents (MeOH, CH_3CO_2H) give different results with the two cations. Both their structure and possible interconversions are under study.

(8) J.E. MAHLER and R. PETTIT, J. Amer. Chem. Soc., 85, 3955 (1963) ; N.A. CLINTON and C.P. LILLYA, J. Amer. Chem. Soc., 92, 3058 (1970).

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