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An unusual epimerization in the diene tricarbonyliron series

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Abstract

A new role for the $Fe(CO)_3$ group as a relay of chemical information rationalizes the unusual epimerization at C_6 of the iron-complexed *erythro*-carbonate (−)-**2**.

The chiral bifunctionalized dienyliron complex (−)-(2*R*, 5*S*) − **1** was used recently for the stereocontrolled preparation of (5*R*, 6*S*)- and (5*S*, 6*S*)-diHETEs (diHydroxyEicosaTetraEnoic acids) [1]. The complexed carbonates **2**, **3** and **4** were key intermediates in these syntheses (Scheme 1).

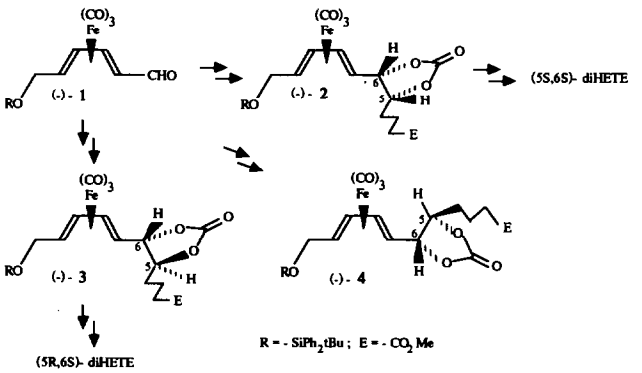
The growing interest in IR-FT spectroscopy for determining the precise location of the binding sites of various ligands [2] led us to envisage the synthesis of the butadienyliron analogues of these diHETEs. This could be achieved providing that the $Fe(CO)_3$ unit is maintained through the sequence of reactions we described previously. During this study, surprising results were obtained in the desilylation step of the two iron carbonate complexes (−)-**2** and (−)-**3**. The purpose of this communication is to describe a quite unusual fluoride-mediated epimerization of the carbon 6 of the *erythro*-carbonate (−)-**2** and to propose a likely rationalization of the epimerization.

The structure of these three iron carbonate complexes *erythro*(−)-**2**, *threo*-(−)-**3**, and (−)-**4**, have been established spectroscopically and confirmed unambiguously by X-ray analysis [3]. Of particular interest is the fact that they are cleanly separated by thin layer chromatography, or even better by HPLC on a 5 μm silica gel column [1].

Desilylation of *erythro*-carbonate (−)-**2** gave two iron-complexed alcohols (−)-**5** and (−)-**6** which were separated by chromatography. They were obtained in *ca.* 1/1 ratios [4*]. Under the same reaction conditions, the *threo*-carbonate (−)-**3** afforded only one iron-complexed alcohol (−)-**7** (Scheme 2).

The structures (−)-**5**, (−)-**6** and (−)-**7** attributed to these three complexes were unambiguously established by silylating [5] them again separately and comparing each silylated compound with our authentic standards (−)-**2**, (−)-**3** and (−)-**4** of known absolute configuration [6*]. Therefore, we conclude that (−)-**5** and (−)-**6** are epimeric at carbon 6, establishing a new epimerization process at this carbon atom close to the iron-complexed moiety during the desilylation of the *erythro*-carbonate (−)-**2** [7*]. It is important to note the key role of the $Fe(CO)_3$ group in this process: desilylation of the free diene corresponding to **2** occurs without epimerization at C_6 atom [1]. The stereochemistry is also important since epimerization does not occur in the case of the *threo*-derivative (−)-**3**.

The mechanism of this unusual epimerization can be tentatively rationalized on the basis of the events depicted in Scheme 3.



Scheme 1.

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* Reference number with asterisk indicates a note in the list of references.

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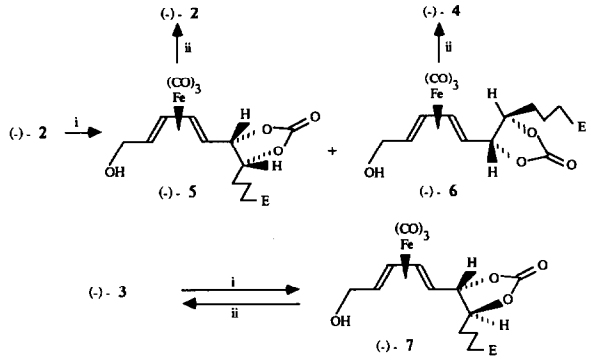
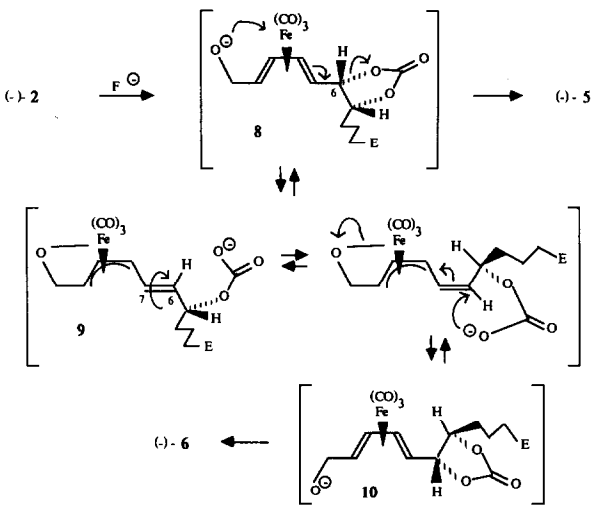


Scheme 2. Reagents and conditions: (i): $^{n}Bu_4NF$, anhydrous THF, −20°C, 1 h (40–70% global yield); (ii): $^{t}BuPh_2SiCl$, anhydrous DMF, imidazole, 20°C, 2 h (90–95%).

These are (a) the classical formation of the alcoholate **8** owing to the strong affinity of fluoride for silicon; (b) intramolecular nucleophilic attack of this alcoholate on the iron atom of **8** [8*]. The breaking of the C_6–O bond follows a new ligand reorganization



Scheme 3.

within the iron coordination sphere leading to conjugated σ-π allyl type intermediate **9**; and (c) the isomerization of the C_6–C_7 bond in **9** as a result of steric decompression of the originally *erythro* system. Recyclization of the carbonate anion *anti* to the organometallic unit affords the epimerized *threo*-carbonate alcohol (−)-**6** via **10**.

In conclusion, besides the well-known stereodirecting and protecting properties of the organometallic unit, this fluoride-mediated long distance (five bonds) epimerization reveals a new relay type property of the $Fe(CO)_3$ group.

References and notes

1 A. Gigou-Barbedette, J.P. Lellouche, J.P. Beaucourt, L. Toupet and R. Grée, *Angew. Chem., Int. Ed. Engl., 28* (1989) 755; J.P. Lellouche, A. Gigou-Barbedette and R. Grée, *Bull. Soc. Chim. Fr., 129* (1992) 605.

2 C. Jaouen, A. Vessières, S. Top, A.A. Ismail and I.S. Butler, *J. Am. Chem. Soc., 107* (1985) 4778; G. Jaouen and A. Vessières, *Pure Appl. Chem., 57* (1985) 1865; S. Tondu, S. Top, A. Vessières and G. Jaouen, *J. Chem. Soc., Chem. Commun.* (1985) 326; P. Pinsard, J.P. Lellouche, J.P. Beaucourt and R. Grée, *J. Organomet. Chem., 354* (1988) 193 and references cited therein.

3 L. Toupet, R. Grée, A. Gigou-Barbedette, J.P. Lellouche and J.P. Beaucourt, *Acta. Crystallogr., C47* (1991) 1173.

4 It is not yet possible to determine the degree of kinetic *versus* thermodynamic control in this epimerization: changing the reaction conditions induced slight preferences for the *threo* derivative (−)-**6** but competitive decomposition processes (including decomplexation) became important.

5 S. Hanessian and P. Lavallée, *Can. J. Chem., 53* (1975) 2975.

6 Spectroscopical data (IR, NMR) are also identical with those of the corresponding standards (ref. 1).

7 It is interesting to note that addition of an excess of CH_3CO_2H or Dowex resin (H^+ form) to reaction medium did not suppress this epimerization; this is consistent with a fast intramolecular process.

8 Such an intramolecular attack of an alcoholate anion has been envisaged in order to explain the lack of reactivity of complexed chlorhydrins towards various basic agents: see J.P. Lellouche, E. Bulot, J.P. Beaucourt, J. Martelli and R. Grée, *J. Organomet. Chem., 342* (1988) C21; see also J.S. Frederiksen, R.E. Graf, D.G. Gresham and C.P. Lillya, *J. Am. Chem. Soc., 101* (1979) 3863.