

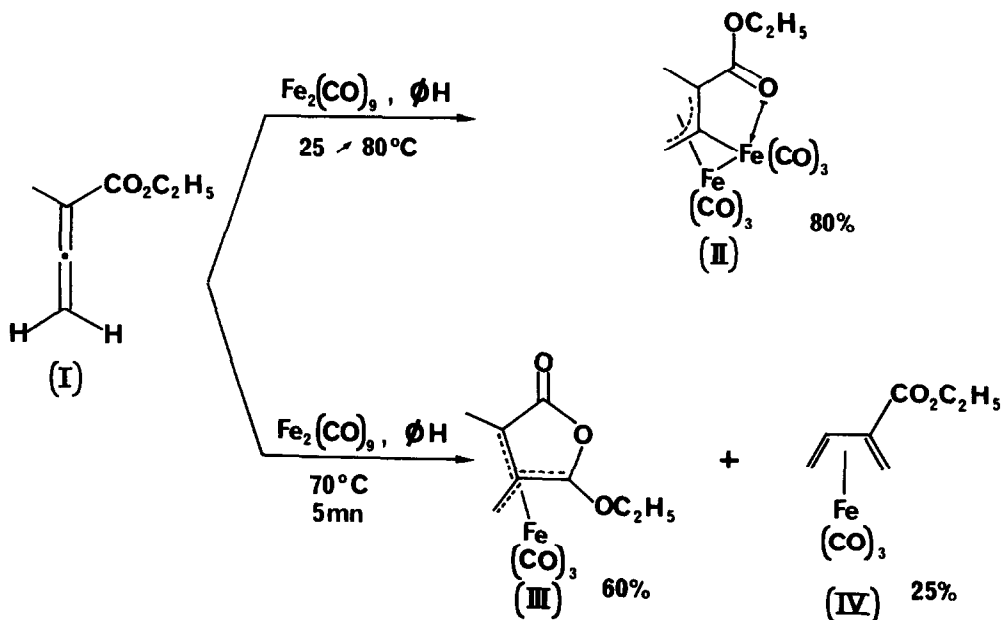
SYNTHESIS OF 2-CARBETHOXY-1,3-BUTADIENE IRONTRICARBONYL STARTING
 FROM AN ELECTROPHILIC ALLENE VIA A TRIMETHYLENEMETHANE COMPLEX.

Francis BRION and Daniel MARTINA

Equipe de Recherche Associée au CNRS n° 687, Institut de Chimie
 de l'Université Louis Pasteur, 1, rue Blaise Pascal, 67008 STRASBOURG, France.

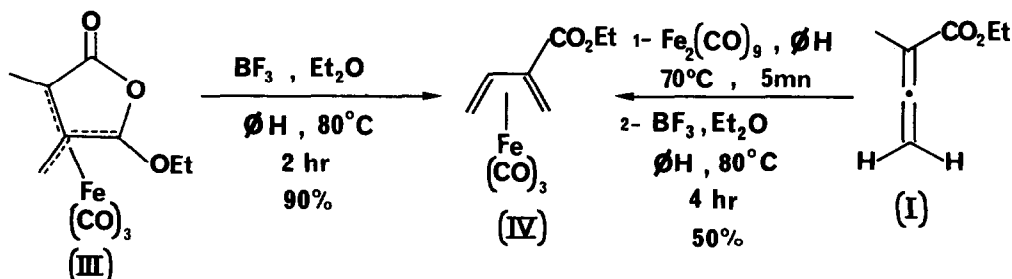
Summary : A new route starting from alkyl allenic esters for the synthesis of 1,3-butadiene
 irontricarboxyl complexes bearing a carbalkoxy group at position 2 is described
 and discussed.

In the preceding paper, we described the structure of two new complexes
 derived from the reaction between the 3-carbethoxy-1,2-butadiene (I) and
 $\text{Fe}_2(\text{CO})_9$ (1). Depending on the experimental conditions, the complexation of
 the allene provides either the binuclear complex (II), or a mixture of the
 new trimethylenemethane complex (III) (formed by carbonylation of the starting
 allene) and the complex (IV).



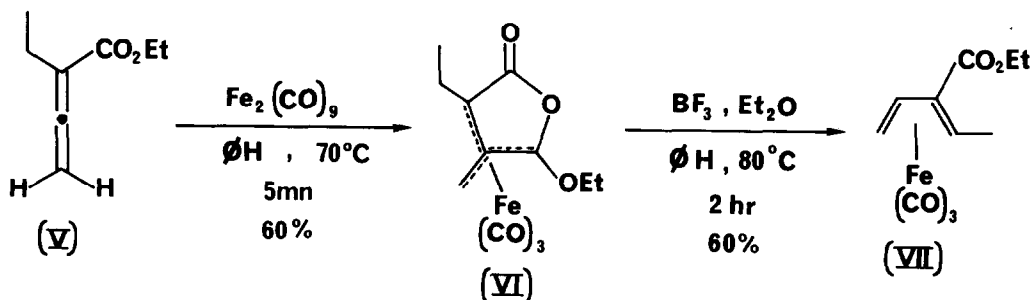
Since no efficient synthesis of the butadienic complex (IV) has been
 published (2), we describe herein a novel rearrangement leading from the
 complex (III) to the complex (IV).

Treatment of a solution of the complex (III) (12.8 mmoles in refluxing benzene (120 ml) with an excess of boron trifluoride etherate (42 mmoles) under Argon for 2 hr provides very easily the butadienic derivative (IV) in good yield (85 %). Furthermore, a direct transformation of the allene (I) (19 mmoles) into the complex (IV) was possible by adding an excess of boron trifluoride etherate (56.5 mmoles) to the crude reaction mixture obtained from $\text{Fe}_2(\text{CO})_9$ (26 mmoles) and the allene (I) (yield : 50 %).



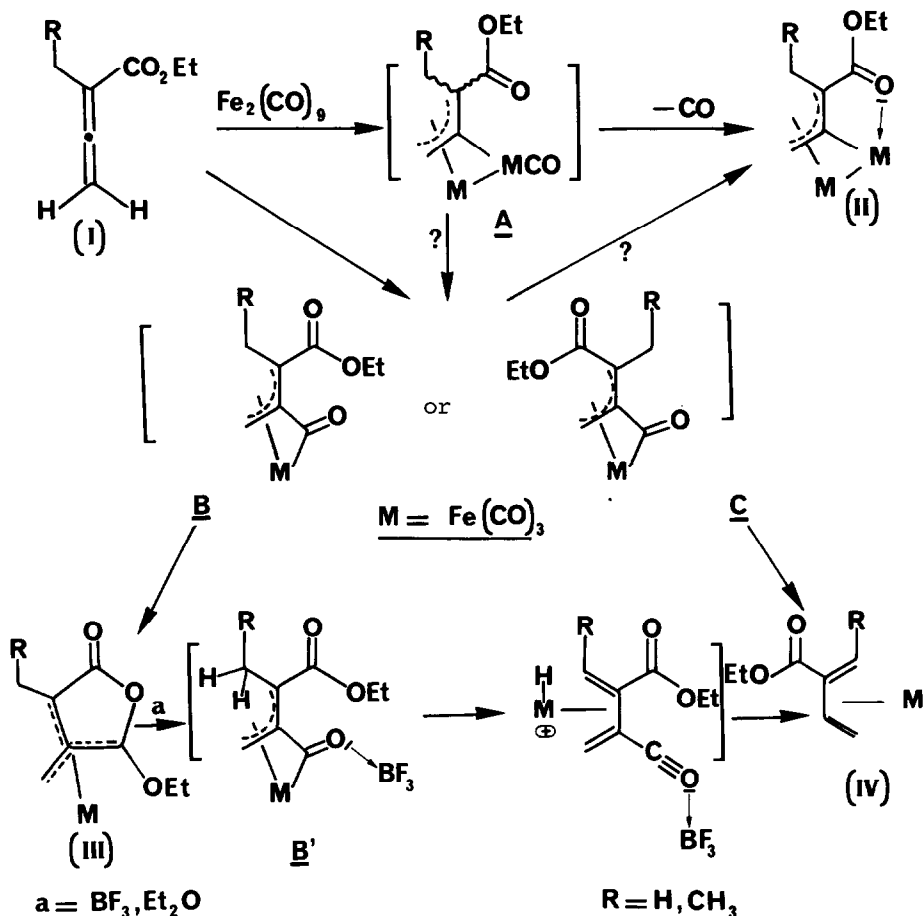
The presence of the Lewis acid ($\text{BF}_3, \text{Et}_2\text{O}$) is necessary for the decarbonylation step [(III) \rightarrow (IV)]. The complex (III), when heated in benzene (80°C) for 2 hr without Lewis acid, either in the presence or absence of $\text{Fe}_2(\text{CO})_9$ remains unchanged. Furthermore, the binuclear complex (II) heated in toluene (110°C) either under a CO pressure (100 psi) or under an Argon atmosphere undergoes no insertion of CO and was recovered unchanged.

In order to understand the formation of the complexes (III) and (IV), we have studied the complexation of the 3-carbethoxy-1,2-pentadiene (V) (3). With the same reaction conditions we obtain here specifically the complexes (VI) and (VII) (4).



In (VI) the ethyl group is still present after complexation, indicating that only the allene moiety reacts during the transformation. The carbonylation reaction is thus analogous to the unusual carbonylation of a η^3 -vinylcarbene iron complex into a $\eta^3 : \eta^1$ (allyl-carbonyl) iron complex observed by Mitsudo and coworkers (5).

We propose therefore the following explanation :



The present carbonylation is however different from that mentioned above (5) by the fact that the CO insertion takes place on the central carbon atom of the π -allyl ligand moiety to give the intermediate of type (B) which can be regarded as trimethylenemethane type complexes. The (B) isomer then undergoes a cyclisation involving the ester group (6) with formation of (III).

The complex (III) which is thermally stable to $80^\circ C$ (2 hr), is then opened in the presence of a Lewis acid possibly through the intermediacy of the BF_3 coordinated acylium bridge complex (B). The resulting activation of the γ hydrogens promotes then the metal assisted [1,3] shift with the subsequent decarbonylation to yield complex (IV).

The direct formation of (IV) during the first reaction, in the absence of BF_3 , Et_2O can in turn be explained by the formation of the anti-isomer C which by necessity cannot cyclise but undergoes a metal assisted [1,3] hydrogen migration to yield (IV).

The new route for the synthesis of 1,3-butadiene iron carbonyl complexes substituted in the 2-position by an ester group which was our goal is consequently a useful synthetic reaction. The striking sequence of carbonylation, decarbonylation and H-migration observed was nevertheless unexpected. A similar reaction sequence has been observed starting from another 3 C di-unsaturated system, i.e. electrophilic cyclopropenes (7). The chemical transformations of this ester function and the study of the chemical properties of the corresponding decomplexed dienes are reported in the subsequent paper of this series (8).

The authors wish to thank Dr. M. Franck-Neumann for helpful discussions. This work was supported by the CNRS (ATP "Catalyse homogène" Décision n° 3792). We are also grateful to the BASF AG for the gift of iron pentacarbonyl.

REFERENCES

All compounds gave satisfactory elementary analysis.

- 1) D. MARTINA, F. BRION, A. DE CIAN, *Tetrahedron Letters*, preceding paper.
- 2) - K.K. JOSHI, *J. Chem. Soc. (A)*, 594, (1966).
 - R.N. GREENE, C.H. DEPUY, T.E. SCHROER, *J. Chem. Soc. (C)*, 3115, (1971).
- 3) G. BUONO, *Tetrahedron Letters*, 3257, (1972).
- 4) Compound VI : yellow crystals $M_p = 58^\circ \text{C}$
NMR (60 and 90 MHz, CDCl_3) δ/TMS : 1.14 ppm (3H,t,J = 7 Hz) ; 1.34 ppm (3H,t, J = 7 Hz) ; between 1.00 ppm and 2.14 ppm (2H,m) ; 3.04 ppm (1H, d,J = 2 Hz) ; 3.20 ppm (1H,d,J = 2 Hz) ; 3.66 ppm (1H,qd,J = 7 Hz and J = 9 Hz) ; 4.24 ppm (1H,qd,J = 7 Hz and J = 9 Hz).
IR (CCl_4) : $\nu_{(\text{C}\equiv\text{O})}$ 2060, 2000, 1990 cm^{-1} ; $\nu_{(\text{C}=\text{O})}$ 1775 cm^{-1} .
Compound VII : yellow oil
NMR (60 MHz, CDCl_3) δ/TMS : 0.45 ppm (1H,dd,J = 9.5 Hz and J = 2.5 Hz) ; 0.94 ppm (1H,q,J = 6.5 Hz) ; 1.35 ppm (3H,t,J = 7 Hz) ; 1.58 ppm (3H,d, J = 6.5 Hz) ; 1.81 ppm (1H,dd,J = 7 Hz and J = 2,5 Hz) ; 4.36 ppm (2H,q, J = 7 Hz) ; 6.00 ppm (1H,dd,J = 9.5 Hz and J = 7 Hz).
IR (CCl_4) : $\nu_{(\text{C}\equiv\text{O})}$ 2050, 1980 cm^{-1} ; $\nu_{(\text{C}=\text{O})}$ 1725 cm^{-1} .
- 5) T.A. MITSUDO, T. SASAKI, Y. WATANABE, Y. TAKEGAMI, S. NISHIGAKI, K. NAKATSU, *J. Chem. Soc., Chem. Comm.*, 252, (1978).
- 6) T.A. MITSUDO, H. WATANABE, T. SASAKI, Y. WATANABE, Y. TAKEGAMI, K. KAFUKU, K. KINOSHITA, K. NAKATSU, *J. Chem. Soc., Chem. Comm.*, 22, (1981).
- 7) M. FRANCK-NEUMANN, C. DIETRICH-BUCHECKER, A. KHEMISS, *Tetrahedron Letters*, (1981), 2307.
- 8) D. MARTINA, F. BRION, *Tetrahedron Letters*, following paper.

(Received in France 19 October 1981)