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STRUCTURES OF TWO COMPLEXES DERIVED FROM AN ALLENIC ESTER AND DI-IRON ENNEACARBONYL. A SYNTHETIC ROUTE TO 2-CARBALCOXY BUTADIENE COMPLEXES.

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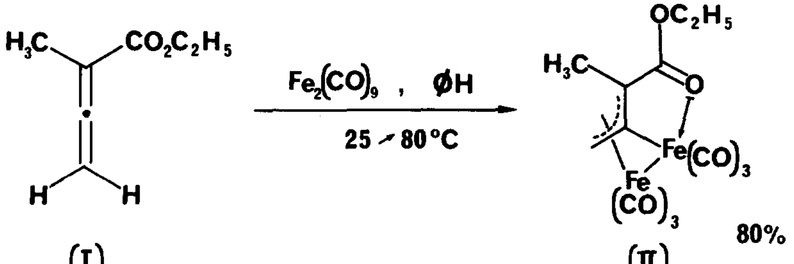
Summary : *The structure of two complexes obtained from the reaction between* $Fe_2(CO)_9$ *and 3-carbethoxy-1,2-butadiene (I) are described.*

The reactions of non-electrophilic allenes with transition metal complexes have been extensively studied (1). With ironcarbonyls, it was shown that these compounds react to give essentially dinuclear complexes (2). Also, many isomerisation reactions of polyunsaturated compounds with transition metals have been described (3). In the case of the tetramethylallene, Gibson and coworkers (4) observed a facile isomerisation into a 1,3-butadienic derivative via a π-allyl ironcarbonyl intermediate.

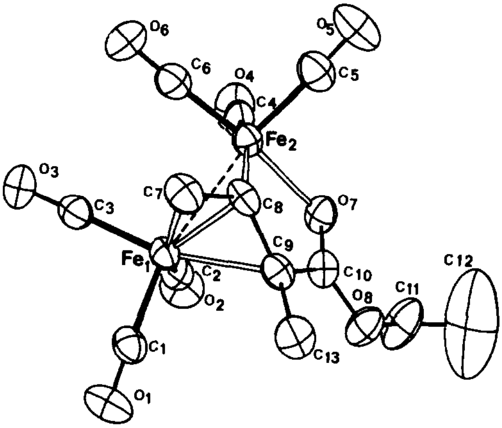
We now report the study of a similar type of isomerisation in the case of an electrophilic allene, disubstituted in the 1-position by an ester and an alkyl group, with the objective of finding a general scheme for the synthesis of 1,3-butadienes solely substituted in the 2-position by such electron withdrawing groups. The 1,3-butadienic derivatives will thus be obtained as stable ironcarbonyl complexes. In fact, it is known that the uncomplexed esters are very reactive and can generally not be isolated as monomers (5).

The 1-carbethoxy-1,2-butadiene (I), readily obtained by known procedures (6) , reacts very rapidly with $Fe_2(CO)_9$ to give different compounds, depending on the experimental conditions. Thus, a slow addition of a solution of (I) (0.50 g, 4 mmoles) in benzene (20 ml) to a suspension of $Fe_2(CO)_9$ (1.90 g, 5.2 mmoles) in benzene (30 ml) under Argon first at room temperature and then heated to 80° C (15 mn) affords only the dinuclear complex (II) (7) (1.29 g, yield : 80 %).



(I) (II)

The molecular structure of (II) has been determined by X-ray analysis ; the complex is analogous to one of the complexes (8) formed in the reaction of propadiene with $Fe_2(CO)_9$, except that one carbonyl ligand is replaced by the ester function which binds through its carbonyl group.



ORTEP drawing of (II). all atoms are represented by 50 % probability thermal ellipsoids.

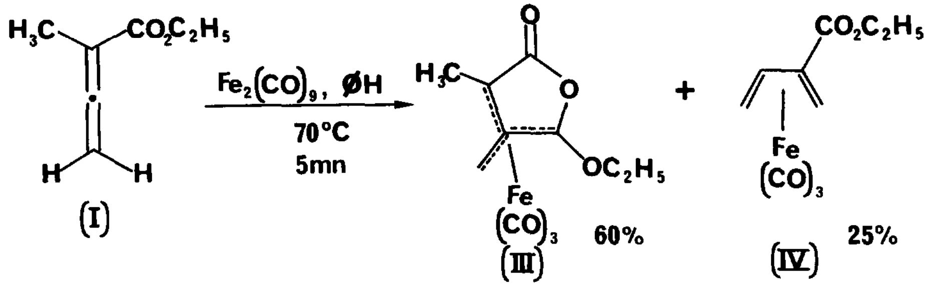
Main distances (Å) are :

Fe_1-Fe_2 : 2.638 (1) ; Fe_1-C_7 : 2.165 (5) ;
Fe_1-C_8 : 1.963 (5) ; Fe_1-C_9 : 2.157 (5) ;
Fe_2-O_7 : 1.998 (3) ; Fe_2-C_8 : 1.949 (5).

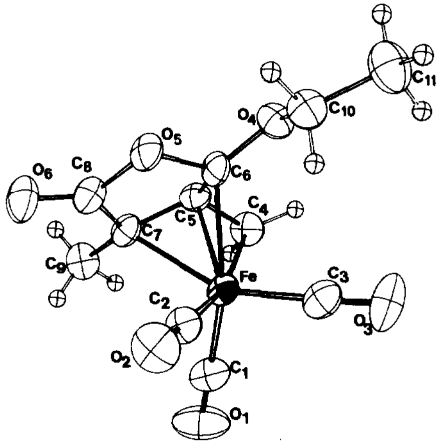
The compound (II) crystallizes in the monoclinic space group $P2_1/C$ with a = 6.638 (3), b = 18.866 (8), c = 12.833 (6) Å, β = 95.85 (6) ; Z = 4, V = 1599 $Å^3$. The calculated density based on four molecules ($Fe_2C_{13}O_8H_{10}$, M = 405.9) per unit cell is 1.68 g/cm^3. The data were collected in the range $2.5° < \theta < 55°$ by a flying step scan technique using Cu Kα radiation on a Philips P.W. 1100 diffractometer. Independent reflections (1427) corrected for absorption were coded as observed $[I > 3\sigma(I)]$. All non-hydrogen atoms were given anisotropic temperature factors that yielded after introduction of the hydrogen atom positions, R = 0.038, Rw = 0.052 (9).

On the other hand, a solution of (I) (0.50 g, 4 mmoles) and $Fe_2(CO)_9$ (1.90 g, 5.2 mmoles) in benzene (50 ml) under Argon when quickly heated at 70° C for five minutes afforded a mixture of the complexes (III) (10)

(0.69 g, yield : 60 %) and (IV) (0.27 g, 25 %) without formation of (II).



As shown by X-ray analysis, the compound (III) is a new cyclic trimethylenemethane complex (11) formed by a carbonylation reaction.



ORTEP drawing of (III). Main distances (Å) and angles (deg.) are :
Fe-C_4 : 2.124 (5) ; Fe-C_5 : 1.956 (4) ;
Fe-C_6 : 2.154 (5) ; Fe-C_7 : 2.180 (4) ;
C_4-C_5-C_6 : 120.7 (4) ; C_4-C_5-C_7 : 122.8 (4) ;
C_6-C_5-C_7 : 102.4 (4).

The compound (III) crystallizes in the monoclinic space group $P2_1/n$ with a = 12.824 (6), b = 6.941 (4), c = 13.983 (7)Å, β = 100.27 (4)° ; Z = 4, V = 1224.8Å^3. The calculated density based on four molecules ($FeC_{11}O_6H_{10}$, M = 293.8) per unit cell is 1.59. Data were collected by using Cu Kα radiation in the range 2.5°<θ<60° with an Enraf-Nonius CAD-4F diffractometer. After correction of absorption 1460 reflections with [I>3σ(I)] were used in refinement (R = 0.059, Rw = 0.069) (9). The spectroscopic data of the known complex (IV) are identical with those previously described (12).

The different experimental conditions used for the formation of complexes between $Fe_2(CO)_9$ and 1-carbethoxy-1,2-butadiene (I) permits thus to direct the reaction to produce either a dinuclear complex (II), or a mixture of the complexes (III) and (IV). The latter result provides a novel method for the synthesis of 2-substituted -1,3-butadienes stabilised as irontricarbonyl complexes.

The following paper describes a new pathway for the synthesis of such isoprenic derivatives (13).

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7) Compound II : red crystals Mp = 65° C
   NMR (250 MHz, C_6D_6) : 0.65 ppm (3H,t,J = 7 Hz) ; 1.01 ppm (3H,s) ; 3.40 ppm (1H,qd,J = 7 Hz and J = 3.5 Hz) ; 3.57 ppm (1H,qd,J = 7 Hz and J = 3,5 Hz) ; 3.61 ppm (1H,s) ; 4.09 ppm (1H,s).
   IR (CCl_4) : 2100, 2070, 2020, 2000, 1985, 1965, 1565 cm^{-1}.
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9) *Tables of fractional coordinates, thermal parameters, values of 10 X Fobs and 10 X Fcalc have been deposited with the Cambridge Crystallographic Data Center.*
10) Compound III : yellow crystals Mp = 78° C
    NMR (250 MHz, $CDCl_3$) : 1.34 ppm (3H,t,J = 7 Hz) ; 1.41 ppm (3H,s) ; 3.10 ppm (1H,d,J = 2 Hz) ; 3.23 ppm (1H,d,J = 2 Hz) ; 3.63 ppm (1H,m) ; 4.20 ppm (1H,m).
    IR (CCl_4) : 2060, 2000, 1990, 1780 cm^{-1}.
11) *For other types of TMM complexes, see for exemple :* J.L. ROUSTAN, A. GUINOT, P. CADIOT, *J. Organomet. Chem.*, 194, *(1980), 191.*
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