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2-CARBETHOXY-1,3-BUTADIENE IRONTRICARBONYL : CHEMICAL TRANSFORMATIONS AND REACTIVITY OF THE CORRESPONDING FREE DIENES.

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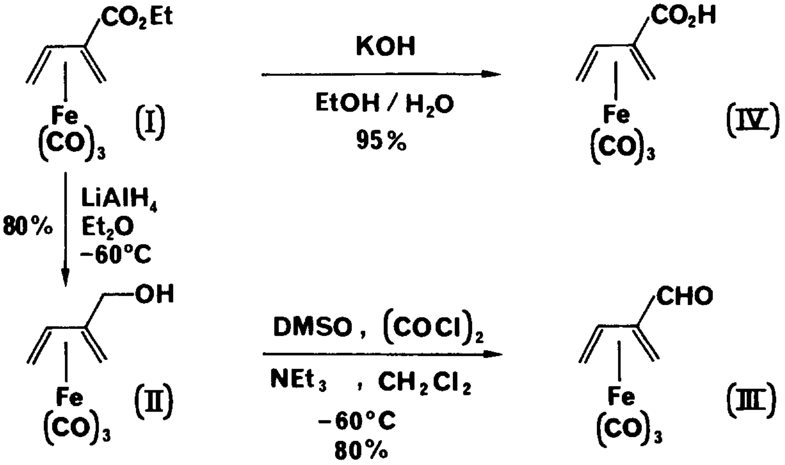
Summary : *Chemical transformations on the 2-carbethoxy-1,3-butadiene irontricarbonyl complex were performed. The dienic and dienophilic reactivities of the corresponding free dienes are studied.*

Recently, new methods of preparation of 1,3-butadienes substituted in the 2-position were described. These compounds can in fact become interesting synthons for the synthesis of terpenic derivatives (1).

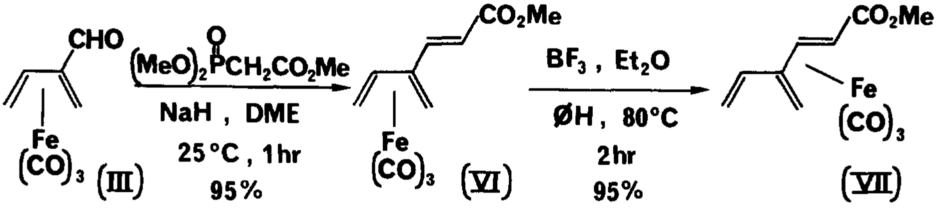
In the preceding paper, we described an easy and direct method for the formation of the stable 2-carbethoxy-1,3-butadiene irontricarbonyl complex (I), starting from an allene (2). Due to the stability of this complex, we were able to carry out chemical modifications on the ester function, as well as to study the free diene reactivity after decomplexation. It is known that 1,3-butadienes substituted in the 2-position with electron withdrawing groups dimerize very easily (3), so that direct transformations cannot be performed.

We have converted the ester (I) into the corresponding acid (IV), alcohol (II) and aldehyde (III) (4) with excellent yields.

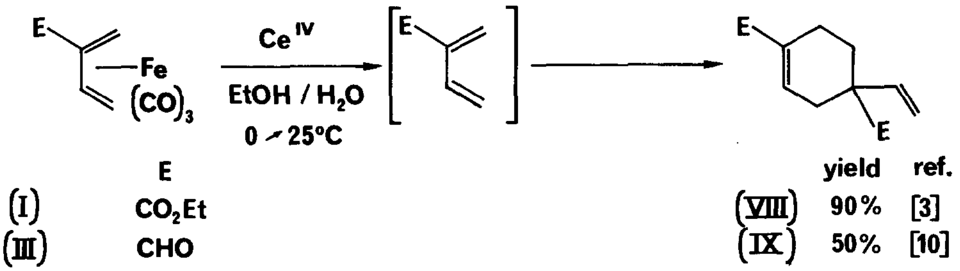


This method seems to be more efficient and generally applicable than those previously reported (1). The methylketone derivative (V) can also readily be obtained as a complex (5).

It is interesting to note that the aldehyde reactivity is seemingly unaffected by complexation : the Horner reaction, using the Wadworth-Emmons conditions (6) affords thus the new 1,3-butadienic complex (VI) isolated in 95 % yield (7). The latter isomerises very easily in the presence of BF_3, Et_2O to give the complex (VII) (8).



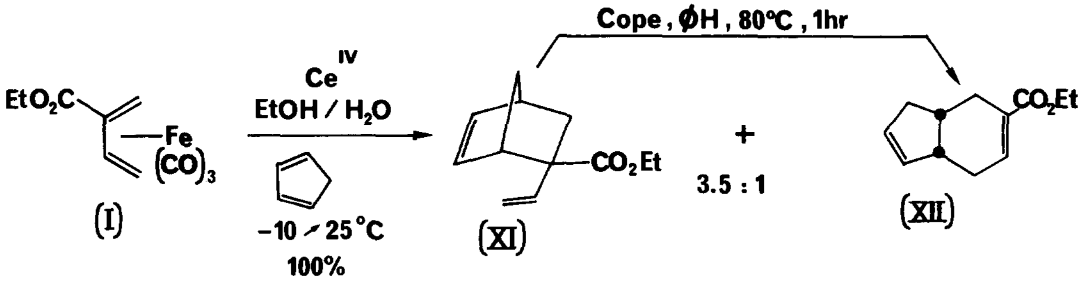
The reactivity of the free dienes was studied by decomplexation using cerium ammonium (IV) nitrate in ethanol. Only the corresponding para Diels-Alder dimers were obtained as shown below.



In the presence of good dienophiles, other authors have observed heteromolecular Diels-Alder additions. The ratio between hetero and homo molecular reactions depends, however, on the mode of production of the diene (1) (3).

In our case however, the decomplexation of (I) in the presence of an excess of dimethyl acetylene dicarboxylate (10 eq.) afforded only the dimer (VIII) as the sole product. This result indicates that this diene has also a strong dienophilic character.

Indeed, the decomplexation of (I) in the presence of an excess of cyclopentadiene afforded specifically the endo adduct (XI) (11), in contrast to the methylketone complex (V) which gave both endo and exo adducts (5). The compound (XI) readily undergoes a Cope rearrangement to the bicyclo [4.3.0.] derivative (XII) (12).



The stereospecificity observed in the case of the ester derivative can be explained by the existence of a greater secondary orbital interaction in the transition state compared to the corresponding ketone compound.

We obtained however only the dimer (VIII) when the decomplexation was performed in the presence of an excess of 2,3-dimethyl-1,3-butadiene (yield : 90 %).

It appears then that the reactivity of the free diene (E=CO_2Et) toward itself as a dienophile is intermediate between the reactivity of cyclopentadiene and 2,3-dimethyl-1,3-butadiene. This reactivity sequence must, however, be interpreted with caution in term of Diels-Alder reactivity since the diene can also be envisaged to react in a radicophilic fashion (13). Further studies of the reactivity of such dienes are in progress.

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All compounds gave satisfactory elementary analysis.

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4) Aldehyde III : yellow crystals Mp = 60° C
NMR (60 MHz, $CDCl_3$) : 0.40 ppm (1H,d,J = 3 Hz) ; 0.78 ppm (1H,dd,J = 10 Hz and 2 Hz) ; 2.14 ppm (1H,dd,J= 7,5 Hz and J = 2 Hz) ; 2.32 ppm (1H,m) ; centered at 5.96 ppm (1H,m) ; 9.78 ppm (1H,s).
IR ($CHCl_3$) : $\nu_{(C\equiv O)}$ 2050,1995, 1980 and $\nu_{(C=O)}$ 1690 cm^{-1}.

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7) Compound VI : yellow crystals Mp = 85° C
NMR ($CDCl_3$, δ/TMS) : 0.20 ppm (1H,d,J = 3 Hz) ; 0.48 ppm (1H,dd,J = 9,5 Hz

and 2,5 Hz) ; 1.91 ppm (1H,dd,J = 7 Hz and 2,5 Hz) ; 2.10 ppm (1H,m) ; 3.77 ppm (3H,s) ; centered at 5.60 ppm (1H,m) ; 6.18 ppm (1H,d,J = 15,5 Hz) ; 7.55 ppm (1H,d,J = 15,5 Hz).

IR ($CHCl_3$) : $\nu_{(C\equiv O)}$ 2050, 1980 cm^{-1} ; $\nu_{(C=O)}$ 1700 cm^{-1} ; $\nu_{(C=C)}$ 1630 cm^{-1}.

) Compound VII : yellow crystals Mp = 41° C

NMR ($CDCl_3$, δ/TMS) : 0.45 ppm (1H,m with J = 3 Hz) ; 1.02 ppm (1H,d, J = 8 Hz) ; 2.31 ppm (1H,m) ; 3.66 ppm (3H,s) ; 5.20 ppm (1H,d,J = 10 Hz) ; 5.58 ppm (1H,d,J = 17 Hz) ; 5.94 ppm (1H,d,J = 8 Hz) ; 6.54 ppm (1H,dd, J = 17 Hz and J = 10 Hz).

IR ($CHCl_3$) : $\nu_{(C\equiv O)}$ 2050, 1995, 1980 cm^{-1} ; $\nu_{(C=O)}$ 1695 cm^{-1}.

) Compound VIII is identical with the dimer described in ref. (3).

) Compound IX : colorless oil

NMR ($CDCl_3$, δ/TMS) : 1.54 to 2.82 ppm (6H,m) ; 5.12 ppm (1H,dd,J = 16 Hz and J = 1 Hz) ; 5.34 ppm (1H,dd,J = 10 Hz and J = 1 Hz) ; 5.80 ppm (1H,dd, J = 16 Hz and J = 10 Hz) ; 6.80 ppm (1H,m) ; 9.34 ppm (1H,s) ; 9.38 ppm (1H,s).

Compound XI : colorless oil (endo refers here to the vinylic group).

NMR ($CDCl_3$, δ/TMS) : 1.22 ppm to 1.36 ppm (2H,m) ; 1.26 ppm (3H,t,J = 7 Hz) ; 1.48 ppm (1H,m) ; 2.51 ppm (1H,dd,J = 12 Hz and J = 4 Hz) ; 2.88 ppm (1H,m) ; 3.32 ppm (1H,m) ; 4.20 ppm (2H,q,J = 7 Hz) ; 4.95 ppm (1H,d,J = 18 Hz) ; 5.01 ppm (1H,d,J = 11 Hz) ; 5.79 ppm (1H,dd,J = 18 Hz and J = 11 Hz) ; 6.02 ppm (1H,m) ; 6.23 ppm (1H,m).

IR (CCl_4) : $\nu_{(C=O)}$ 1720 cm^{-1} ; $\nu_{(C=C)}$ 1630 cm^{-1}.

Compound XII : colorless oil

NMR ($CDCl_3$, δ/TMS) : 1.28 ppm (3H,t,J = 7 Hz) ; 1.92 ppm to 2.16 ppm (3H,m) ; 2.34 ppm to 2.62 ppm (4H,m) ; 2.87 ppm (1H,m) ; 4.18 ppm (2H,q, J = 7 Hz) ; 5.56 ppm (1H,m) ; 5.66 ppm (1H,m) ; 7.11 ppm (1H,m).

IR (CCl_4) : $\nu_{(C=O)}$ 1700 cm^{-1} ; $\nu_{(C=C)}$ 1655, 1630 cm^{-1}.

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