

Preliminary communication

STEREOCHEMICAL LEAKAGE MECHANISMS FOR TRICARBONYL-(DIENYL)IRON CATIONS

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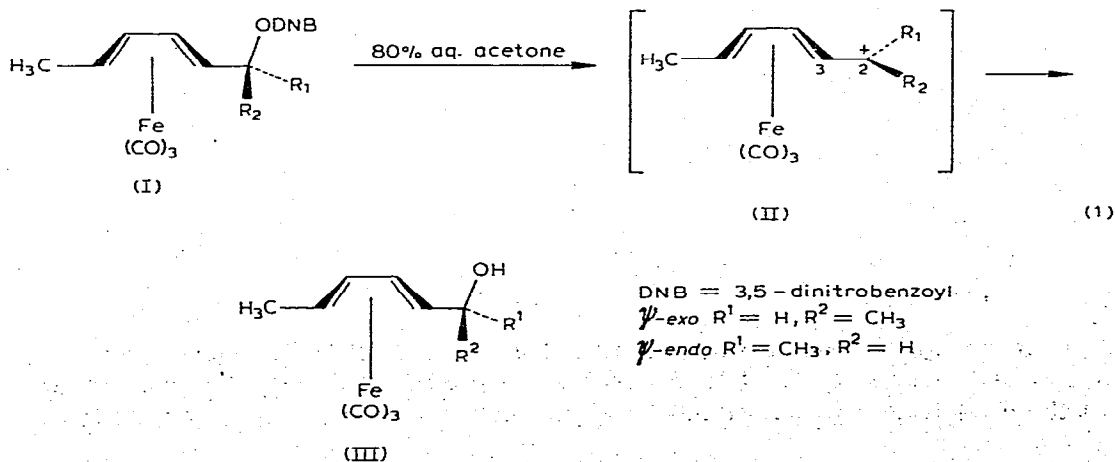
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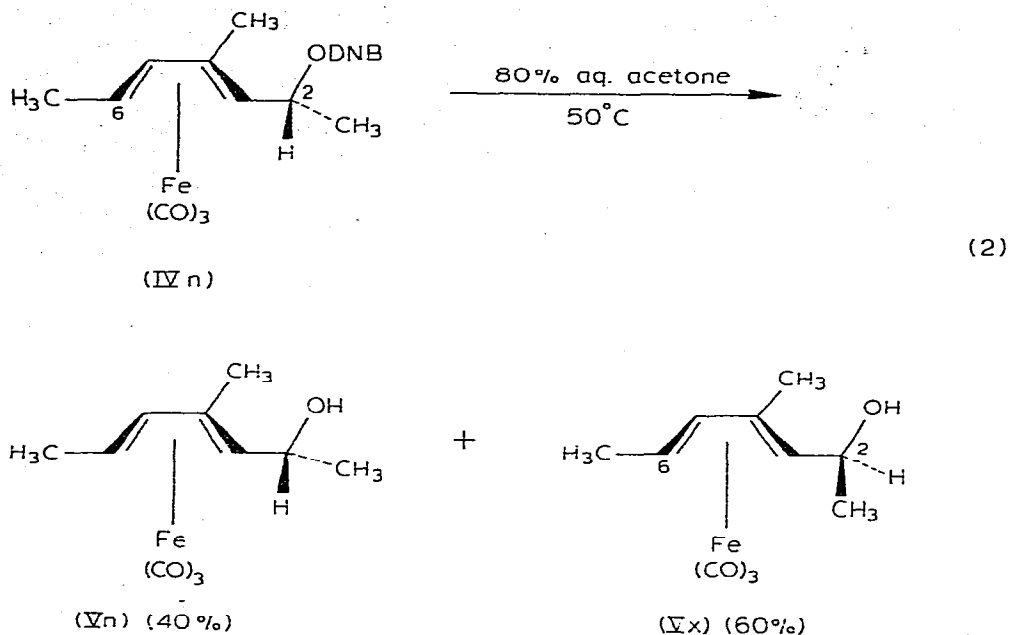
Summary

ψ -Endo to ψ -exo leakage during solvolysis of a ψ -endo-dienol- $\text{Fe}(\text{CO})_3$ dinitrobenzoate ester does not proceed via a *syn,syn-cis*-dienyl- $\text{Fe}(\text{CO})_3$ cation. The most probable leakage mechanism involves non-stereospecific ionization of the dinitrobenzoate ester. *syn,syn-cis*-Dienyl- $\text{Fe}(\text{CO})_3$ cations are formed from a ψ -exo-dienol- $\text{Fe}(\text{CO})_3$ complex during chromatography on grade I neutral alumina.

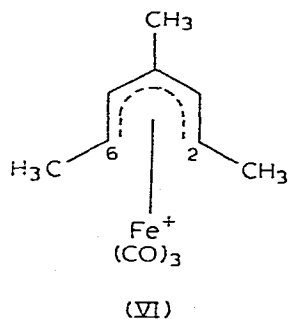
Solvolysis of dienyl ester- $\text{Fe}(\text{CO})_3$ complexes normally proceeds stereospecifically via *trans*-dienyl- $\text{Fe}(\text{CO})_3$ cations, to give alcohols of the same configuration (eq. 1) [1].



The ψ -*exo*-ester which bears a methyl group at C(4) (IVx) also solvolyzes with retention of configuration, but its slow solvolyzing epimer IVn reacts with considerable leakage to ψ -*exo*-alcohol Vx (eq. 2) [2].



Leakage could proceed via a *syn,syn-cis*-dienyl-Fe(CO)₃ cation (VI) since these cations are known to produce ψ -*exo*-alcohols on hydrolysis [1,3]. This leakage mechanism has been tested by solvolysis of ester IVn labeled with a deuterium atom at C(2). Intervention of VI would cause scrambling of the label between positions 2 and 6 which are equivalent by symmetry in VI.



Reduction of the corresponding ketone with NaBD₄ in ethanol gave Vn-d₂ stereospecifically* [2]. Esterification produced IVn-d₂. Saponification of the ester to give unscrambled Vn-d₂ ruled out scrambling during esterifica-

*Synthetic procedures have been previously described [2]. Physical properties of the deuterium labeled compounds were identical to those previously reported with obvious exceptions such as missing ¹H NMR signals.

tion. A sample of ester was solvolyzed in degassed 80% aqueous acetone under nitrogen at 50°C in the presence of one equivalent of sodium 3,5-dinitrobenzoate to give a clean mixture of 40% Vn- d_2 and 60% Vx- d_2 *. Separation on silica gel with Skellysolve B/CH₂Cl₂ eluent gave pure samples of the epimeric alcohols with no detectable scrambling of the deuterium label (see Table 1). These observations clearly rule out formation of cation VI during solvolysis.

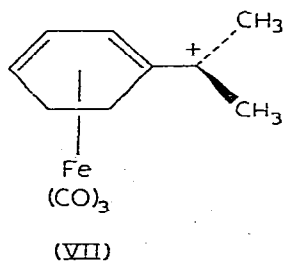
TABLE 1
DEUTERIUM LABELING DATA

| Sample | %- d at C(2) ^a | Total label ^b (% of one atom d) |
|---|-----------------------------|--|
| Vn- d_2 from NaBD ₄ reduction | >80 | 83 |
| Vn- d_2 from saponification of IVn- d_2 | 85 | |
| Mixture of Vx- d_2 and Vn- d_2 from solvolysis | 86 | |
| Pure Vn- d_2 from solvolysis | 87 | |
| Pure Vx- d_2 from solvolysis | 85 | 83 |
| Vx- d_2 resubjected to solvolysis conditions for 68 h | 84 | |

^aFrom NMR integration (\pm 3-4%). ^bFrom mass spectral analysis.

Cation VI can be generated under mild conditions however. A previous attempt to separate the solvolysis product mixture by chromatography on grade I neutral alumina with pentane/CH₂Cl₂ eluent gave unscrambled ψ -endo-alcohol Vn- d_2 and completely scrambled ψ -exo-alcohol (1:1 Vx- d_2 and Vx- d_6). No interconversion of the ψ -exo- and ψ -endo-alcohols occurred on the column. Our subsequent results (see above) make it clear that scrambling occurred on the alumina column. Similar results were obtained by alumina chromatography of a Vn- d_2 /Vx- d_2 mixture produced by treating 4-methyl-3,5-heptadien-2-ol- d_2 with Fe₂(CO)₉. Scrambling of the deuterium label in ψ -exo-alcohol is most easily understood as the result of formation of VI. Scrambling of the label in Vx under conditions where no scrambling in Vn or Vx/Vn interconversion occurs is consistent with the high ψ -exo/ ψ -endo-solvolysis-rate ratio of 2500 observed for IVx and IVn [2].

Finally, solvolysis of IVn- d_2 in unbuffered 80% aqueous acetone at 65°C for 72 h produced Vn- d_2 but ψ -exo alcohol which was $29 \pm 4\%$ Vx- d_6 . Di-



*Quantitative analysis by NMR integrations of the distinct 4-methyl signals.

nitrobenzoic acid formed during solvolysis presumably catalyzes ionization of the relatively reactive $Vx-d_2$, which leads to formation of cation VI.

Our results leave non-stereospecific ionization of IVn or rotation about the C(2)—C(3) bond in the intermediate *trans*-dienyl—Fe(CO)₃ cation (e.g. II) as the most likely mechanisms for stereochemical leakage during solvolysis. Recent results show that the latter process is slow in VII at +10°C on the NMR time scale [4]*, while we have recently observed non-stereospecific ionization of ψ -endo-alcohol Vn in FSO₃H [6]. Thus, until positive evidence for facile C(2)—C(3) rotation is obtained, non-stereospecific ionization must be considered the most probable mechanism.

Acknowledgments

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References

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*A referee has pointed out that the necessity of rotating a methyl past the Fe(CO)₃ group in VII should slow rotation. Unfortunately the ion with one methyl replaced by H rearranged on warming [4] so no information on this more relevant model exists. In the related ferrocenyl-methylcarbinyl cation (Fc $\dot{C}HCH_3$) the barrier to rotation about the ring-carbinyl carbon bond is high, $E_a = 20$ kcal/mole [5].