Thermal Decomposition of Tricarbonyliron Lactone Complexes

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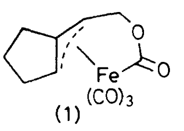
Summary Tricarbonyliron lactones, on warming in tetrahydrofuran or benzene, afford products derived from decarbonylation, decarboxylation, and rearrangement pathways.

AN isolated report suggested that thermal decomposition of tricarbonyliron lactone complexes occurs *via* initial decarbonylation and rearrangement.[1] Here we show that a number of other pathways are also possible.

Complex (**1**) was warmed to reflux in tetrahydrofuran (THF), and after 3 h the enal (**2**) (24%) and the diene complex (**3**) (54%) could be isolated by preparative layer chromatography. While (**2**) could reasonably be derived from decarbonylation and rearrangement of (**1**) the major product (**3**) must arise from decarboxylation.



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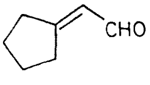

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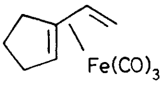

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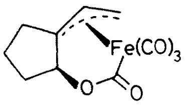

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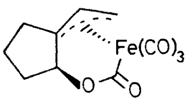

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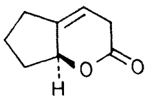

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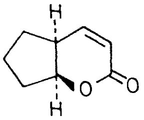

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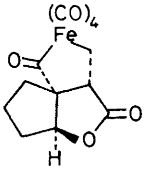
The spectral properties of (**2**) show structurally significant absorptions at ν_{max} 1670 and 1650 cm^{-1} and at δ 9·72 (1H, d, *J* 8 Hz). The tricarbonyliron diene complex (**3**) was compared with an authentic sample prepared by treatment of the uncomplexed diene with $Fe_2(CO)_9$.

In a similar experiment, the *syn*-tricarbonyliron lactone (**4**)[2] in boiling THF (or benzene) gave a 40% yield of (**3**) as the only isolable product after $2\frac{1}{2}$ h. However, the *anti*-isomer (**5**)[2] in THF afforded (**3**) (30%), and the two δ-lactones (**6**) and (**7**) in 16 and 40% yield respectively. While (**6**) compared well with authentic material[2] (**7**) showed structurally significant spectroscopic properties at ν_{max} 1720 cm^{-1}, δ 6·9 (1H, dd, *J* 10 and 5·5 Hz), 5·93 (1H, d, *J* 10 Hz), 4·95 (1H, m), and 2·6—1·6 (7H, m).

On warming the *anti*-isomer (**5**) at 70 °C in benzene for 12 h, it was possible to isolate a 7% yield of (**3**) together with (**6**) (9%), (**7**) (50%), and a novel iron complex (**8**) (5%), m.p. 119—122 °C, ν_{max} 2100, 2020, 1760, and 1675 cm^{-1}, δ 4·77 (1H, br, s), 3·18 (1H, dd, *J* 7·8 and 8·5 Hz), 2·76 (1H, dd, *J* 7·8 and 11 Hz), 2·63 (1H, dd, *J* 8·5 and 11 Hz), and 1·99—1·6 (6H, m). The structure of (**8**) was confirmed by *X*-ray crystallography.[3]



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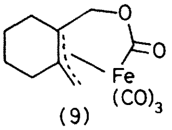

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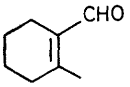

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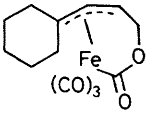

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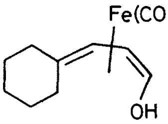

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The lactone complex (**9**), in benzene at 60 °C, gave the enal (**10**) in 69% yield on oxidative work up with trimethylamine *N*-oxide.[4] We have so far not been successful in isolating possible intermediate tricarbonyliron enal complexes.

Finally, on warming (**11**) in THF, a single tricarbonyliron dienol complex (**12**)[5] was obtained in 82% yield, the structure of which was assigned from its spectral properties (ν_{max} 3605, 2940, 2875, 2040, and 1980—1880 cm^{-1}, δ 5·12 (1H, d, *J* 7·6 Hz), 3·52 (1H, m, D_2O exch.) 3·38—2·3 (6H, m), and 2·3—1·2 (6H, m).

These examples clearly show that a number of pathways operate in the thermal decomposition of tricarbonyliron lactone complexes.

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[1] R. Aumann, K. Fröhlich, and H. Ring, *Angew. Chem., Int. Ed. Engl.*, 1974, **13**, 275.

[2] (a) G. D. Annis, S. V. Ley, and R. Sivaramakrishnan, *J. Organomet. Chem.*, 1979, **182**, C11; (b) G. D. Annis, S. V. Ley, C. R. Self, and R. Sivaramakrishnan, *J. Chem. Soc., Perkin Trans.* 1, accepted for publication.

[3] We thank Prof. D. Rogers and Dr. D. J. Williams for this result, full details of which will appear later.

[4] Y. Shvo and E. Hazum, *J. Chem. Soc., Chem. Commun.*, 1974, 336.

[5] For other examples of dienol complexes see C. H. DuPuy and C. R. Jablonski, *Tetrahedron Lett.*, 1969, 3989.