

Novel Rearrangement of an (η^4 -2-Pyrone)iron Complex

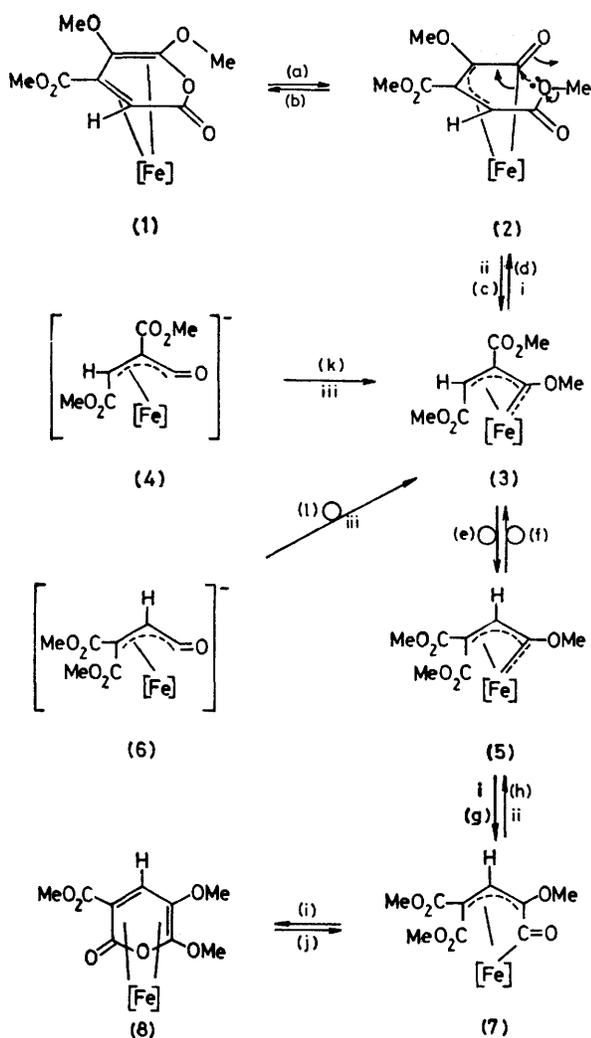
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Summary (Tricarbonyl)(η^4 -5,6-dimethoxy-4-methoxycarbonyl-2-pyrone)iron (**1**) rearranges thermally to tri-carbonyl(η^4 -5,6-dimethoxy-3-methoxycarbonyl-2-pyrone)iron (**8**) and the structures of (**1**) and (**8**) have been

determined by X-ray analyses; a mechanism involving (η^3 -vinylcarbene)iron complexes and a novel 1,4-oxygen shift reaction are proposed for the rearrangement.

THE rearrangement of organic ligands in organometallic complexes is an important factor which determines the structure and the distribution of the products in reactions using organometallic compounds.¹ We now report a novel rearrangement of an (η^4 -2-pyrone)iron complex (**1**) to its



SCHEME. [Fe] = Fe(CO)₃, i, CO, ii, -CO, iii, SFO₂(OMe).

† Satisfactory analytical data for the complexes have been obtained; **1**: m.p. 67 °C, *M* 330 (354.1); i.r. (KBr) 2070 vs, 2010 vs, 1995 vs, 1975 vs, 1760 s, and 1730 s cm⁻¹; ¹H n.m.r. [(CD₃)₂CO] τ 6.02(OMe, s), 6.06(OMe, s), 6.14(OMe, s), and 7.08 (=C-H, s); ¹³C n.m.r. (Me₄Si, CDCl₃) δ 38.4 (=C-H, d, *J*_{CH} 171.9 Hz), 53.4 (OMe, q, *J*_{CH} 147.9 Hz), 59.3 (OMe, q, *J*_{CH} 147.9 Hz), 60.6 (OMe, q, *J*_{CH} 147.9 Hz), 78.2 (C-CO₂Me, s), 119.5 (C-OMe, s), 127.7 (C-OMe, s), 166.3 (C=O, s), 168.6 (C=O, s), and 206.5 (FeC=O, br). **8**: m.p. 143 °C, *M* 406 (354.1); i.r. (KBr) 2084 vs, 2018 vs, 1994 vs, 1770 s, and 1718 s cm⁻¹; ¹H n.m.r. (CDCl₃) τ 3.90 (=C-H, s), 6.09 (OMe, s), and 6.23 (OMe \times 2, s); ¹³C n.m.r. (Me₄Si, CDCl₃) δ 45.7 (s, C-CO₂Me), 52.8 (OMe, q, *J*_{CH} 146.5 Hz), 56.6 (OMe, *J*_{CH} 146.5 Hz), 58.8 (OMe, *J*_{CH} 146.5 Hz), 68.2 (=C-H, d, *J*_{CH} 183.6 Hz), 121.7 (C-OMe, s), 123.7 (C-OMe, s), 164.1 (C=O, s), 168.0 (C=O, s), 202.3, 203.9, and 210.1 (FeC=O, s).

‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

isomer (**8**) (Scheme), which was found in the course of our study of the reaction of an (η^3 -vinylcarbene)iron complex (**3**) with carbon monoxide.

The reaction of (tricarbonyl)[1-3- η -*trans*-1-methoxy-2,3-bis(methoxycarbonyl)prop-2-en-1-ylidene]iron² (**3**) with carbon monoxide at 80 atm in dichloromethane at 25 °C for 12 h afforded yellow crystals of FeC₁₂H₁₀O₉ (**1**) in a yield of 79% after evaporation of the solvent. Furthermore, heating the highly purified complex (**1**) in 1,2-dichloroethane at 58 °C for 12 h in an atmosphere of carbon monoxide gave yellow crystals of FeC₁₂H₁₀O₉ (**8**), the isomer of (**1**), in a yield of 21%. Although the spectroscopic data of the products[†] suggested that (**1**) and (**8**) were derivatives of the (η^4 -2-pyrone)iron complexes, the final structure could not be determined so single-crystal X-ray diffraction studies on (**1**) and (**8**) were performed.

Crystal data: (**1**) C₁₂H₁₀FeO₉, *M* = 354.05, orthorhombic, space group *Pbca*, *a* = 13.104(1), *b* = 19.646(2), *c* = 11.346(2) Å, *Z* = 8, *D*_m = 1.607 g cm⁻³, *D*_c = 1.6107(3) g cm⁻³. Least-squares calculations on 1741 non-zero independent reflections (Mo-K α radiation) gave an *R* value of 5.3%. (**8**) C₁₂H₁₀FeO₉, monoclinic, space group *P2₁/a*, *a* = 11.151(1), *b* = 18.021(2), *c* = 7.103(1) Å, β = 101.20(1)°, *Z* = 4, *D*_m = 1.700 g cm⁻³, *D*_c = 1.6797(4) g cm⁻³. Least-squares calculations on 2393 non-zero independent reflections gave an *R* value of 5.0%. The results, shown in the Figure, indicate that (**1**) and (**8**) are (tricarbonyl)(η^4 -5,6-dimethoxy-4-methoxycarbonyl-2-pyrone)iron and (tricarbonyl)(η^4 -5,6-dimethoxy-3-methoxycarbonyl-2-pyrone)iron, respectively.‡

Although η^4 -2-pyrone metal complexes are known,³ (**1**) and (**8**) are the first examples of 2-pyrone complexes with fully determined molecular structures. The characteristic of the molecular structures of (**1**) and (**8**) is that the bond lengths between the iron atom and the terminal carbons of the butadiene moiety [Fe-C(4) and Fe-C(7), 2.03–2.08 Å] are shorter than those found in the derivatives of (butadiene)Fe(CO)₃ (2.09–2.14 Å),⁴ which may be ascribed to the effect of the 2-pyrone ring itself rather than to the substituents on the ring because both (**1**) and (**8**) show the same tendency.

The reaction path of the formation of (**1**) from (**3**) can reasonably be inferred as follows. The fact that a 1-4- η -vinylketen complex (**10**) is formed⁵ in the carbonylation of (**9**) (equation 1) strongly suggests that (**1**) is derived from the corresponding vinylketen complex (**2**) by the intramolecular reaction of the ester group at the 'anti' position with the acyl-iron group. Taking into account the molecular geometry of (**2**) and the fact that the reverse reaction (step a, Scheme) readily occurs, one possible mechanism would be the nucleophilic attack of the methoxy group of the ester on the acyl-carbon of the keten group followed by methyl transfer from the methoxycarbonyl group to the acyl-oxygen [Scheme, (**2**)].

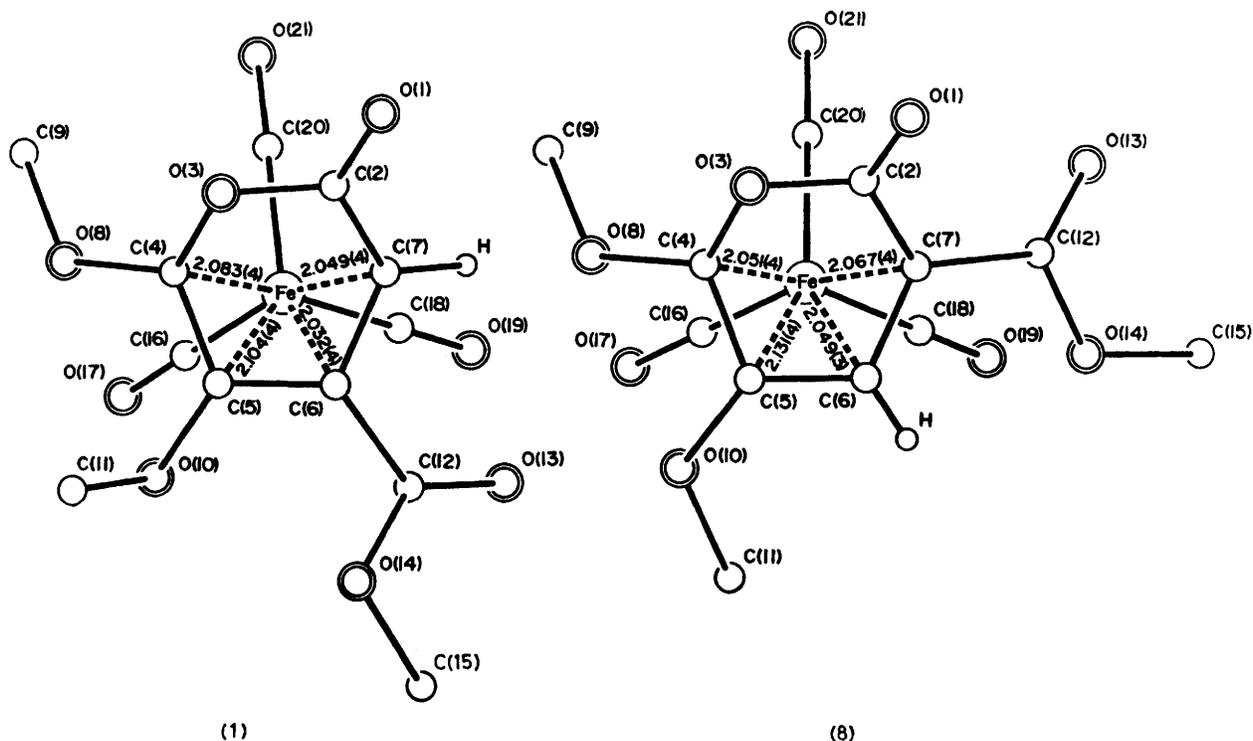
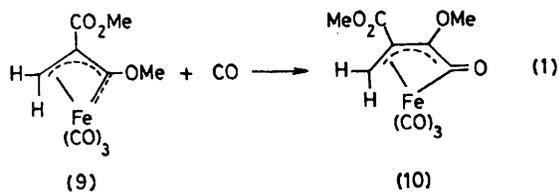
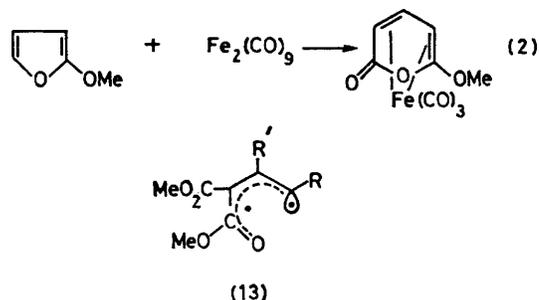


FIGURE. Molecular structures of (1) and (8). Important distances (Å) and angles (°) are [(1), (8)] C(4)-C(5) 1.423(6), 1.447(5), C(5)-C(6) 1.408(6), 1.391(4), C(6)-C(7) 1.457(6), 1.447(5), C(4)-O(3) 1.430(5), 1.431(5), C(2)-O(3) 1.368(5), 1.367(4), C(2)-C(7) 1.461(6), 1.493(5), Fe-C(16) 1.788(5), 1.784(4), Fe-C(18) 1.824(4), 1.827(4), Fe-C(20) 1.796(5), 1.795(4); C(4)-C(5)-C(6) 112.3(4), 111.1(3), C(5)-C(6)-C(7) 113.3(4), 114.8(3).



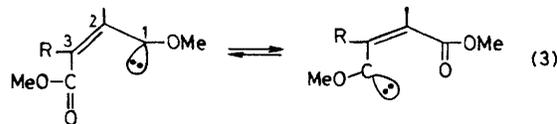
The results of the X-ray analyses show, to our surprise, that (1) rearranges to (8) under mild reaction conditions. Concerning this rearrangement the following facts have been observed. (i) The complex (1) does not rearrange to (8) under 60 atm pressure of carbon monoxide. This strongly suggests the presence of a decarbonylation process in the rearrangement. (ii) The thermal decomposition of (1) to (3) in CDCl_3 at 60 °C under an argon atmosphere was confirmed by i.r. and ^1H n.m.r. spectra. (iii) Usually, an η^3 -vinylcarbene complex is prepared by the reaction of the corresponding η^3 -acryloyl-iron complex with $\text{SFO}_2(\text{OR})$ as shown in the reaction path k in the Scheme. However, the methylation of the complex (6) does not give the corresponding vinylcarbene complex (5) but instead gives (3), derived by the rearrangement of a methoxycarbonyl group at the 'syn' position in (6). Treatment of (6) with $\text{SFO}_2(\text{OCD}_3)$ selectively gave (11). The complex obtained by the methylation of (6) had been erroneously assigned to be (5).⁶



From these observations the mechanism of the rearrangement of (1) to (8) can be rationalized as shown in the Scheme. First, (1) decomposes to (3) by the decarbonylation of the vinylketene complex (2). Complex (3) rearranges to (5) which reacts with carbon monoxide to give (8) via an η^4 -vinylketene complex (7). Assuming that all

the processes are equilibria, the formation of (8) from (1) can be explained. The rearrangement of (3) to (5) may reasonably be explained by assuming the formation of an unstable (η^1 -2,5-dimethoxyfuran)iron complex (12), derived from nucleophilic attack on the carbene carbon by the oxygen atom of the carbonyl group of the methoxycarbonyl group at the 'anti' position in (3) and subsequent fission of the O-C(5) bond of the furan ring (Scheme) affording the rearranged η^3 -vinylcarbene complex (5). This mechanism is supported by the fact that the reaction of 2-methoxyfuran with $\text{Fe}_2(\text{CO})_9$ gives (η^4 -6-methoxy-2-pyrone) $\text{Fe}(\text{CO})_3$ (equation 2),⁷ and also by the formation of furans in the photolysis of diazomalonate in acetylenes which proceeds via a biradical (13),⁸ the valence tautomer of the vinyl carbene ligand of the complex (5). Alternatively, during the rearrangement between (3) and (5) an intramolecular

oxidation-reduction reaction may occur with the methoxycarbene being oxidized to a methoxycarbonyl group and the methoxycarbonyl group being reduced to a methoxycarbene group. Thus, the rearrangement of (1) to (8) could involve a novel 1,4-oxygen shift or 1,4-carbene transfer in the rearranging ligand (equation 3).



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