3-Methoxybuta-1,3-dienone(tricarbonyl)iron. A Novel Carbonylation and a Stabilised Vinylketen

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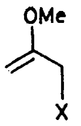
Summary The reaction of 2-methoxyallyl chloride (**1a**) and nonacarbonyldi-iron affords 3-methoxybuta-1,3-dienone-(tricarbonyl)iron (**4**), while the corresponding bromide (**1b**) and iodide (**1c**) form the π-allyl complexes (**2b**) and (**2c**), respectively; 2-methoxy-π-allyl(tricarbonyl)iron chloride (**2a**) can be obtained from 1-chloro-2-methoxypropene (**3a**) and nonacarbonyldi-iron.

The 2-methoxyallyl halides (**1a**—**c**) represent a simple and hitherto unknown class of bifunctional compounds, which have been obtained recently for the first time.[1] We describe here the reactions of (**1a**—**c**) with nonacarbonyldi-iron.

The iodide (**1c**) (1 g) in benzene (50 ml) was stirred under nitrogen with $Fe_2(CO)_9$ (1 g) for 3 h at room temperature.

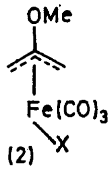
Chromatography on silica (benzene eluant) gave brown crystals of the iodide (**2c**)† (15%), m.p. 57°.

Under the same conditions the bromide (**1b**) (1 g) containing *ca.* 0·3 g 1-bromo-2-methoxypropene (**3b**)[1] and $Fe_2(CO)_9$ gave the bromide (**2b**)† (*ca.* 5%), orange crystals, m.p. 67°, and a trace of a second compound.



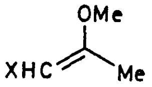
(1)

(a; X = Cl)
(b; X = Br)
(c; X = I)



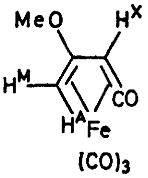
(2)

(a; X = Cl)
(b; X = Br)
(c; X = I)

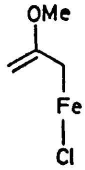


(3)

(a; X = Cl)
(b; X = Br)



(4)



(5)

The second compound formed in this reaction was the major product when the chloride (**1a**) (5 g) and $Fe_2(CO)_9$ (3 g) were heated in benzene (30 ml) to 40° for 1 h. The product, bright yellow, volatile crystals (*ca.* 10%), had m.p. 59°, δ (CS_2; Me_4Si) 1·47 (H^A), 2·91 (H^M), and 3·52 (H^X) (clean AMX pattern, J_{AM} 4·7, J_{MX} 3, J_{AX} 1 Hz), and 3·69s (3H, s) p.p.m.; ν_{max} (C_6H_6) 2060vs, 2000vsbr, 1960w, 1775s, 1405w, 1340m, 1205w, 1060m, 965m, and 865m cm^{-1}; *m/e* 238, 210, 182, 154, and 126. On the basis of this information the new compound is 3-methoxybuta-1,3-dienone(tricarbonyl)iron (**4**), which is a complexed vinylketen‡ and must have been formed in a novel carbonylation, possibly *via* (**5**), which instead of losing carbon monoxide and forming the π-allyl complex (**2a**) might prefer to lose Cl^- and to suffer migratory insertion to give (**4**). Clearly, the balance of competing reactions is sensitive to the halogen and it is interesting that the chloride (**2a**), whilst not being formed from (**1a**), is obtainable from the isomeric 1-chloro-2-methoxypropene (**3a**).[1] Thus, treatment of (**3a**) [prepared by redistilling a mixture of (**1a**) + (**3a**)] with $Fe_2(CO)_9$ under standard conditions did not yield any (**4**), but instead yellow crystals of (**2a**),† m.p. 72°, which remained unchanged when exposed to carbon monoxide under pressure.

In conclusion, whatever the detailed mechanism and scope of the reactions described it seems clear that the organic ligand of (**4**) joins the growing number of reactive intermediates which can be modified and stabilised by bonding to a transition metal.

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† All new compounds (**2a**—**c**) gave satisfactory C and H analyses, and spectral data, and a molecular ion in the mass spectrometer, together with characteristic fragments due to, *inter alia*, successive loss of three carbonyl groups and loss of halogen.

‡ Vinylketens have been implicated as transitory intermediates in the electrocyclic opening of cyclobutenones[2] and one derivative, namely perchlorobuta-1,3-dienone has been detected in an i.r. cell on photolysis of perchlorocyclobutenone at −196°.[2b] A complexed trimethylated vinylketen, in which the position of one methyl group is unknown, has been obtained by a completely different route several years ago; see R. B. King, *Inorg. Chem.*, 1963, **2**, 642.

[1] G. Greenwood and H. M. R. Hoffmann, *J. Org. Chem.*, 1972, **37**, 611.
[2] (a) E. F. Jenny and J. D. Roberts, *J. Amer. Chem. Soc.*, 1956, **78**, 2005; (b) O. L. Chapman and J. D. Lassila, *ibid.*, 1968, **90**, 2449; (c) J. E. Baldwin and M. C. McDaniel, *ibid.*, p. 6118.