Friedel–Crafts Chemistry of Tricarbonyldieneiron Complexes: Carbonylative Annulation of Tricarbonylmyrceneiron

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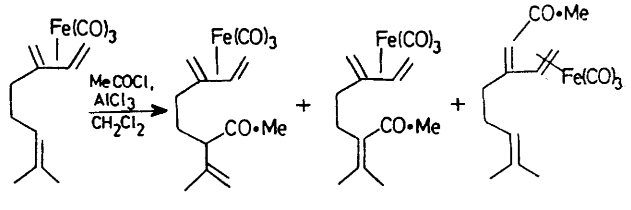
Summary A novel annulation of tricarbonylmyrceneiron (**1**) into (**6**) has been achieved using oxalyl chloride and aluminium chloride at −78 °C in dichloromethane.

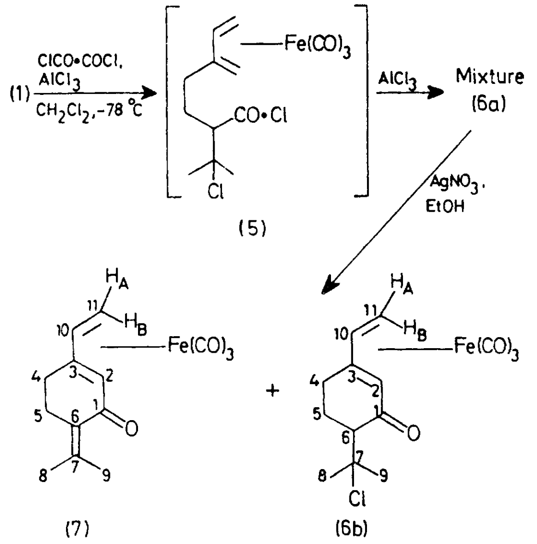
DURING studies of the chemistry of tricarbonyldieneiron complexes we investigated the reactions of functionalities present as a substituent on the diene ligand. Combination of the chemistry of such groups with that of the diene–$Fe(CO)_3$ portion leads to some interesting possibilities, one of which is discussed in the present paper. Here we have chosen to investigate the reactions of a free carbon–carbon double bond using the readily available tricarbonylmyrceneiron complex (**1**), a limited amount of chemistry of which is already documented.[1]

Preliminary studies showed that (**1**) reacted instantaneously at −78 °C with an acetyl chloride–aluminium chloride Perrier complex in dichloromethane to produce (**2**) as the major product, together with a small amount of (**3**), showing the $Fe(CO)_3$ to act as a protecting group for the diene. At 0 °C, however, several products were obtained, among which were (**2**), (**3**), and (**4**), the latter resulting from acetylation of the diene–$Fe(CO)_3$ group in the known



(1) (2) (3) (4)

manner.[2] These compounds were identified by i.r., ^{1}H and ^{13}C n.m.r., and mass spectrometry. Such behaviour prompted an investigation of the reaction between oxalyl chloride–aluminium chloride and (**1**), since this reagent is known to decarbonylate and produce, after aqueous work-up, carboxylic acids.[3] Addition of a solution of (**1**) in dichloromethane to an excess of oxalyl chloride and aluminium chloride (in a mole ratio 1 : 2, previously mixed at room temperature) in dichloromethane at −78 °C, led to instantaneous reaction, as evidenced by a darkening in colour. Immediate aqueous work-up and extraction with dichloromethane, followed by preparative t.l.c. (benzene, silica) afforded a single yellow band in 35—40% yield. ^{1}H N.m.r. spectroscopy indicated this to be a mixture of two compounds, and the presence of a monochloride derivative of formula $C_{14}H_{15}ClFeO_4$ was indicated in the mass spectrum (*M* 328·0009, chloride indicated by *M* and *M* + 2 abundances). These compounds could not be separated chromatographically, but treatment with ethanolic silver nitrate at room temperature led to precipitation of silver chloride and the formation of compounds (**6b**) and (**7**) which were separated by preparative t.l.c. [benzene–ethyl acetate (10 : 1), silica] and the structures of which were assigned on the basis of i.r., ^{1}H, and ^{13}C n.m.r. spectroscopy, and mass spectrometry.† A consideration of the spectral and chemical information for the mixture obtained earlier suggests that the two compounds (**6a**) present are diastereoisomeric chlorides probably formed *via* the intermediate (**5**), only one of which loses HCl on reaction with silver nitrate to produce (**7**), the other isomer (**6b**) remaining unchanged. The stereochemistry of the single pure isomer has not yet been assigned. Although chlorides were not obtained during acetylation reactions of (**1**), they are known products of Friedel–Crafts acylation of olefins[4] and may arise here owing to the less basic nature of the C=O oxygen in the carbonium ion intermediate leading to (**5**), as compared to that in acetylation intermediates, preventing intramolecular deprotonation [*cf.* (**1**) → (**2**)].



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† Spectral data for (**6b**) and (**7**): (**6b**), pure single isomer recrystallised from light petroleum, m.p. 91—93 °C (decomp.); ν_{max} ($CHCl_3$) 2050 and 1970 cm^{-1} [$Fe(CO)_3$], 1665 cm^{-1} (C=O); δ ($CDCl_3$), ^{1}H: 5·42 (1H, t, *J* 8 Hz, H-10), 3·3—1·9 (total 5H, m, H_2-4, H_2-5, and H-6), 1·77 (1H, dd, *J* 8 and 2 Hz, H_A), 1·76 (3H, s) and 1·52 (3H, s), 2 × Me, 1·42 (1H, s, H-2), and 0·32 (1H, dd, *J* 8 and 2 Hz, H_B); ^{13}C: 209·337 (s) and 203·488 (s) [$Fe(CO)_3$ and C-1], 110·511 (s, C-3), 82·462 (d, C-10), 72·722 (s, C-7), 57·788 (d) and 56·749 (d) (C-6 and C-2), 38.049 (t, C-11), 33·374 (q) and 28·049 (q) (C-8 and C-9) and 27·789 (t) and 26·491 (t) (C-4 and C-5) p.p.m.; *M* 328·0009. (**7**), m.p. 100—103 °C (decomp.); ν_{max} ($CHCl_3$) 2050 and 1980 [$Fe(CO)_3$], 1640 (C=O), and 1600sh (C=C): δ ($CDCl_3$), ^{1}H: 5·34 (1H, t, *J* 8 Hz, H-10), 3·10—2·30 (4H, H_2-4 and H_2-5), 1·98 (3H, s) and 1·70 (3H, s) (2 × Me), 1·78 (1H, dd, *J* 8 and 3 Hz, H_A), 1·56 (1H, s, H-2), and 0·42 (1H, dd, *J* 8 and 3 Hz, H_B); ^{13}C: 209·462 and 197·514 [$Fe(CO)_3$ and C-1] 146·224 and 131·939 (C-6 and C-7), 110·642 (C-3), 82·332 (C-10), 59·606 (C-2) 37·659 (C-11), and 27·789, 27·400, 23·244, and 22·595 (C-4, C-5, C-8, and C-9); *M* 302·0250.

[1] D. V. Banthorpe, H. Fitton, and J. Lewis, *J.C.S. Perkin I*, 1973, 2051; R. B. King, T. A. Manuel, and F. G. A. Stone, *J. Inorg. Nuclear Chem.*, 1961, **16**, 233; D. Dell, N. Maoz, and M. Cais, *Israel J. Chem.*, 1969, **7**, 783.

[2] R. E. Graf, and C. P. Lillya, *J. Amer. Chem. Soc.*, 1972, **94**, 8282; E. O. Greaves, G. R. Knox, and P. L. Pauson, *Chem. Comm.*, 1969, 1124.

[3] P. E. Sokol, *Org. Synth.*, 1964, **44**, 69.

[4] J. K. Groves, *Chem. Soc. Rev.*, 1972, **1**, 73.