Tricarbonyliron Deactivation of a Cycloheptatriene Towards Electrophilic Attack

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Summary Treatment of tricarbonylditropyliron with tetracyanoethylene proceeds by addition to the unco-ordinated ring followed by addition to the co-ordinated ring.

CO-ORDINATION of dienes[1,2] and trienes[3] to tricarbonyliron has permitted a study of the electrophilic chemistry of these systems. The role of the metal in these reactions is still not fully understood. While there is evidence that stabilization of intermediates is important[1,3] it is not clear whether the metal activates or deactivates the olefin.

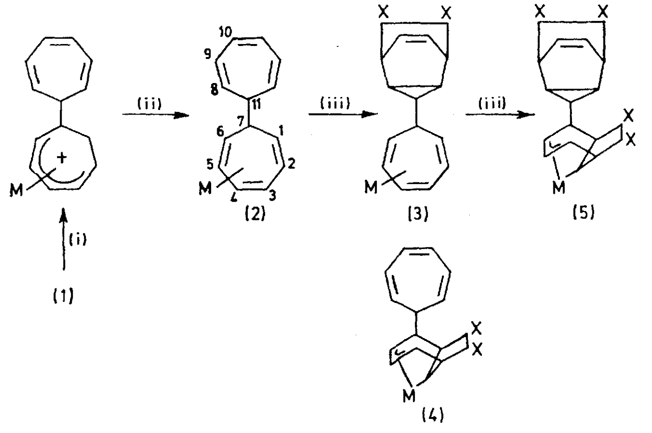

FIGURE. M = Fe(CO)$_3$, X = (CN)$_2$, Reagents; (i) $C_7H_7BF_4$; (ii) OH$^-$ and silica gel; (iii) TCNE.

Cycloheptatriene[4] and its tricarbonyliron complex[5] (**1**) both react with tetracyanoethylene, TCNE, the former by 1,4-addition and the latter by *exo* 1,3-addition. It was decided to attempt a comparison of these two reactions within the same molecule. For this purpose the ditropyl system (**2**) was synthesised as illustrated.† The structure assigned to (**2**) is in agreement with its n.m.r. spectrum;‡ τ 3·4 (2H, t, J 4 Hz, 10-H), 3·7—4·9 (8H, m, 1-, 2-, 4-, 5-, 8-, 9-H), 7·0 (3H, m, 3-, 6-, 7-H), 8·2 (1H, q, J 6 Hz, 11-H). While it is possible that the assignment of 11-H and 7-H could be reversed the alternative structures with the C_7H_7 group substituting the 1 and 6 positions, respectively, (which could only be formed by loss of an *endo* proton) are not consistent with the n.m.r. spectrum.

Treatment of (**2**) with a molar quantity of TCNE gave an off-white solid (**3**) in more than 80% yield. A sample of (**3**) was found to react with an excess of TCNE to give (**5**). The position of addition in (**3**) and (**5**) can be deduced from their i.r. spectra by comparison with (**1**) and the known adduct of (**1**) with TCNE.[5] The electron-withdrawing cyanide groups cause a marked increase in the absorption position (*ca.* 30 cm^{-1}). This effect is absent in (**3**) and observed in (**5**). As (**4**) was not detected in the reaction of (**2**) there is a deactivation of the co-ordinated ring in (**2**) which is greater than would be expected for steric reasons alone. However, the ready formation of (**5**) demonstrates that reaction at the co-ordinated ring is not precluded. Further related studies on intermolecular competition reactions are in progress.

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† All new compounds gave satisfactory elemental analysis.

‡ 60MHz, in CS_2, with $SiMe_4$ as internal reference.

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