Cation-radicals: Metal-catalysed Cyclodimerisation of Aromatic Enamines

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WE have shown[1] that *N*-vinylcarbazole (I) can be cyclodimerised in methanol to *trans*-1,2-di-carbazol-9-ylcyclobutane[2](Ia) under the influence of iron(III) and cerium(IV) salts. The most effective were nitrates and perchlorates, both readily hydrolysed by the solvent to give active catalysts of unknown composition, presumably containing methoxide and hydroxide ligands. On account of the acid produced by this hydrolysis there was significant concurrent acid-catalysed methanolysis of (I) to give 9- (1-methoxyethyl)-carbazole.

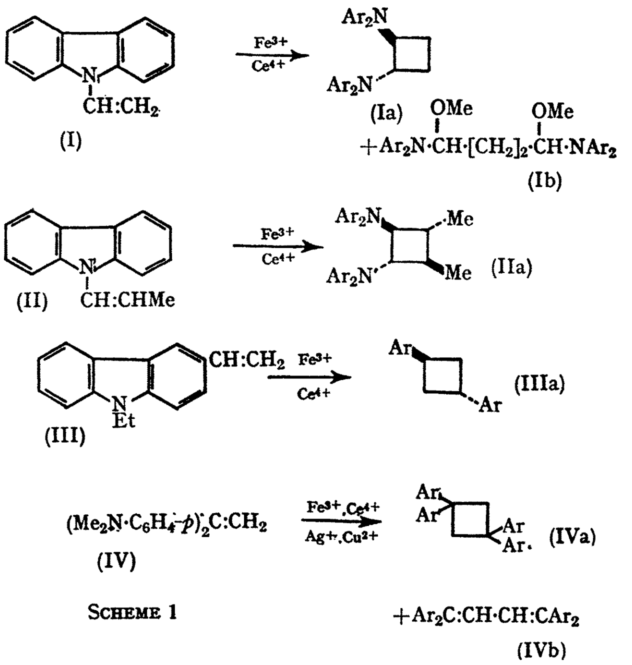
A more detailed study has shown that in the presence of a three-fold molar excess of 2,2′-bipyridyl (over Fe^{3+}), the reaction is greatly slowed (not inhibited as previously reported) but the yield of cyclobutane is increased to 60—70%. Furthermore, with or without bipyridyl, another dimer is formed in yields which vary with the molar ratio [*N*-vinylcarbazole]/[Fe^{3+}] up to a maximum of 17% [based on (I)] This second dimeric species was identified as 1,4-dicarbazol-9-yl-1,4-dimethoxybutane (Ib) from its molecular weight and n.m.r. and i.r. spectra. Kinetic studies have established that the rate of formation of the cyclobutane in the presence of an excess of bipyridyl is given by $d[Ia]/dt = k_2[Fe^{3+}][N\text{-vinylcarbazole}]$, where $k_2 = 9{\cdot}3 \times 10^{-4}$ l. mole^{-1} sec.$^{-1}$ at 25° and $E_a = 26$ kcal. mole.$^{-1}$.

This cyclodimerisation is a general and efficient reaction of aromatic enamines in methanol solution (examples are shown in Scheme 1). For the enamines (II)—(IV) concurrent methanolysis of the vinyl group was insignificant and the products were recovered in yields averaging 90% of the starting olefin. With the 1,1-diarylethylene (IV) the product was a mixture of the cyclobutane (IVa) and the butadiene (IVb) depending on the catalyst and the initial [olefin]/[catalyst] ratio. Cyclobutane formation is genuinely *catalytic* as indicated by the following typical reaction mixture: (IV) in methanol (10^{-2}M) with $Cu(NO_3)_2,3H_2O$ in methanol (10^{-5}M) gave a 90% yield of cyclobutane (IVa) in *ca.* 15 min. at room temperature. With this enamine almost all copper(II) salts are effective, especially those of organic acids [*e.g.* copper(II) heptanoate]. For all the enamines, solvent effects are dramatic and yields of cyclobutane are inevitably reduced and sometimes eliminated in solvents other than methanol. Other workers have shown[3] that with (I), iron(III) nitrate in solvents other than methanol leads to rapid cationic polymerisation.

The *N*-vinyl-enamines (I) and (II) give 1,2-disubstituted cyclobutanes (head-to-head dimerisation) whereas the *C*-vinyl-enamines (III) and (IV) yield 1,3-disubstituted cyclobutanes (head-to-tail dimerisation).[†] During reactions of (I) and (II) with Fe^{3+} or Ce^{4+}, free-radical species are involved as indicated by the efficient free-radical copolymerisation of (I) and (II) with added methyl methacrylate. In contrast, copolymerisation (or homopolymerisation) of methyl methacrylate with the enamines (III) and (IV) was not observed under similar reaction conditions.

Dimerisation of the enamines is possibly related to the relative redox potentials of the olefin and metal catalyst, [*e.g.* (I) is unaffected by Cu^{2+} under the reaction conditions] and since aromatic amines readily undergo one-electron transfer reactions, it is reasonable to postulate cation-radicals as intermediates in the cyclodimerisations.

Formation of the dimethoxybutane (Ib) and the butadiene (IVb) are to be expected[4,5] from dimerisation of the enamine cation-radical to the appropriate butane dication (Scheme 2). The latter would be expected to be solvolysed in the case of



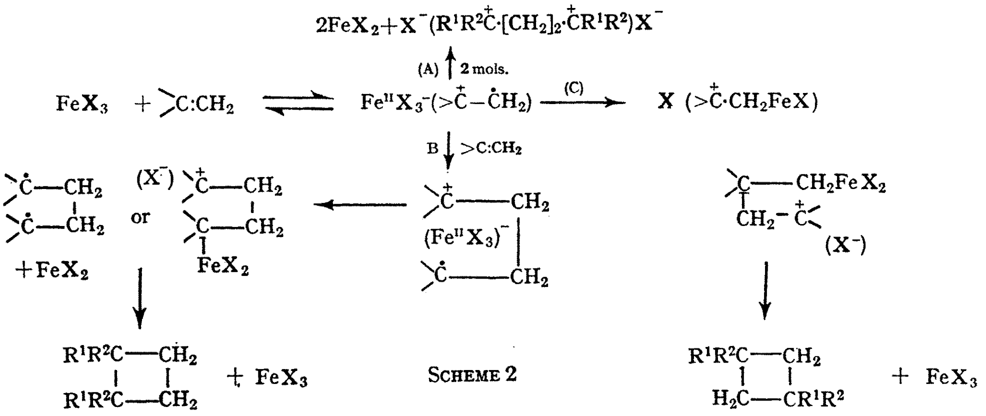
SCHEME 1

[†] Characterisation of the stereochemistry of the cyclobutanes was achieved by n.m.r. analysis, details of which will be given in the full paper. (See also ref. 2).

(I) and to eliminate in the case of (IV). It is expected that small amounts of related open-chain dimers would be formed during reactions of (II) and (III), but so far these have not been isolated.

Intramolecular rearrangement of the initial redox ion-pair (reaction C) would lead to a reactive organometallic derivative which could react with an excess of enamine to give only the head-to-tail dimer. This path appears to be followed by enamines (III) and (IV) which would be expected to form solvolytically stable *p*-aminobenzyl cations. The mechanism is consistent with the absence of free radicals during reactions of these two olefins. Cations from the *N*-vinyl compounds (I) and (II) are much less stable and would be expected to associate more closely with their appropriate complex metal counterion. Thus free-radical reactivity of the cation radical would be expected (reaction B), leading to the observed head-to-head addition. This reaction pathway is consistent with the observed free-radical copolymerisation of methyl methacrylate.

In a related study[5] Szwarc and his collaborators have isolated $MeOCPh_2{\cdot}CH_2{\cdot}SbCl_4$ from the oxidative coupling of 1,1-diphenylethylene with $SbCl_5$ as oxidant. Several different reaction paths may be envisaged for formation this compound but an attractive one corresponds with reaction C in Scheme 2.



SCHEME 2

Cation-radicals have been suggested[6] as intermediates in other reactions of enamines and our results indicate that free-radical or cationic activity may be utilised according to reaction conditions. It is evident that catalytic cyclodimerisation of certain olefins may be a highly efficient process under very mild conditions.

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