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3-AMINO-2,4-DIFERROCENYLCROTONITRILE, THE SUPPOSED FERROCENYLKETENIMINE

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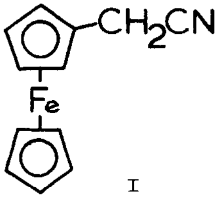
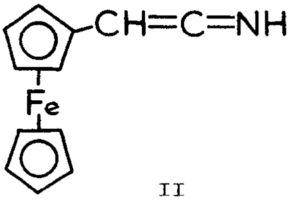
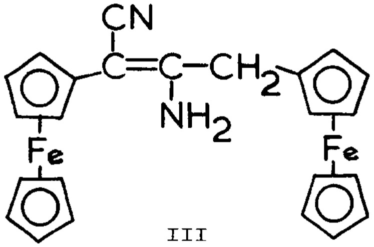
Dewey[1] observed that ferrocenylacetonitrile (I) fails to add a methyl group on treatment with MeMgCl, but gives instead an 'isomer', m.p.144-147°. He formulated this as the ketenimine (II) although no other ketenimines with free NH group are known, and the compound did not revert to the cyanide tautomer. One of us (S.T.) had independently obtained this compound and we assumed from the known[2] stability of the ion $(C_{10}H_9FeCHCN)^-$ and previous examples[3] of abnormal behaviour of cyanides with Grignard reagents, that the product is dimeric and results from a Thorpe condensation.



I



II



III

The dimeric formulation is confirmed by the mass spectrum which includes strong parent peaks at 450,0474 ($C_{24}H_{22}Fe_2N_2$ requires 450.0481), 451.0519 ($C_{23}{}^{13}CH_{22}Fe_2N_2$ requires 451.05145) as well as P^{2+} ions m/e 225.0226 (calc. 225.02405) and 225.5271 (calc. 225.5257). We formulate the product as the enamine (III), a structure which is in much better agreement with all the spectral data than structure (II). The i.r. peak at 2185 cm^{-1} (which is too weak and too high frequency for C=C=N) is the CN stretch and a peak at 1635 cm^{-1} can be assigned to C=C stretch. The multiplicity of N-H peaks reported[1] is due to solid state effects, as only two broader peaks (at 3490 and 3395 cm^{-1}) appear in saturated CCl_4 solution. The u.v. spectrum [λ_{max} (EtOH) 203, 252, 290, 335 (sh) and 442 nm] is comparable with that of vinylferrocene[4] and the n.m.r. spectrum may now be assigned as follows: δ 3.56, CH_2 (not -CH=), 4.75, NH_2 (disappears in D_2O); the 18H multiplet at δ 4.18 includes two triplets, one at 4.32 and one (partly obscured) at 4.18 as expected for the C=C substituted ring.

Although the compound showed surprising resistance to attempted acylation or hydrolysis, we believe that the above evidence demands the rejection of structure (II) and justifies proposal of the alternative (III).

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