Thermal Sigmatropic Rearrangements in Macrocyclic Pyrrolic Nickel Complexes

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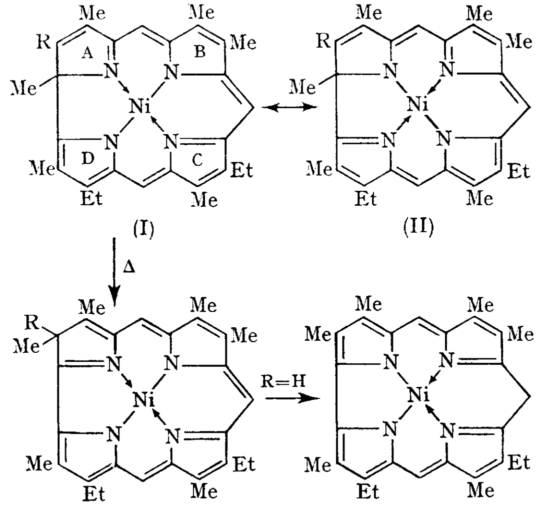
THE nickel 1-methyltetradehydrocorrins (*e.g.*, I)[1] have the conjugation of the organic ligand broken by the C-1 angular methyl group, and it seemed possible that, under suitable conditions, these compounds might rearrange to more stable conjugated derivatives.

When the nickel complexes (I) were heated under reflux in *o*-dichlorobenzene for 30 min., they gave isomeric neutral complexes. Three examples (I; R = Me, Et, and H) have been studied. The structures of the rearranged products (III; R = Me, Et) in the first and second examples were established on the basis of their n.m.r. and mass spectra. Thus the n.m.r. spectrum of (III; R = Et) showed that one ethyl group with the methyl triplet at τ 9·8 differed markedly from the other two. One of the methyl groups (singlet at τ 8·6) also differed from the others suggesting that an ethyl and a methyl group were substituents at a saturated carbon atom. In the analogous product (III; R = Me) two methyl groups were associated with a singlet at τ 8·6 in the n.m.r. spectrum. The presence of geminal alkyl groups was confirmed by the mass spectra of the products in which the base peaks resulted from loss of an alkyl radical from the parent ion. The thermal rearrangement of (I; R = H) was carried out in order to interrelate the nickel 1-methyltetradehydrocorrins and the nickel corroles (*e.g.*, IV).[2] The electronic spectrum of the rearranged product was identical with that of a nickel corrole, and showed the characteristic spectral shift after

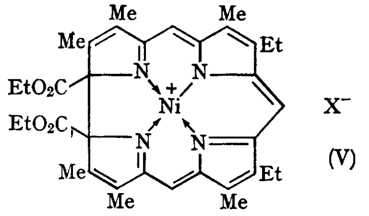


(I) (II) (III) (IV)

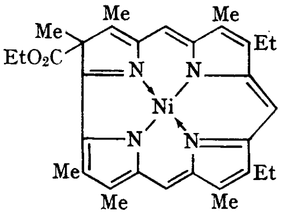
treatment with base, indicating that the 2,2-disubstituted corrole (III; R = H) was less stable than its tautomer (IV). The yield of the nickel corrole (IV) was low due to a further thermally induced transformation which is at present under investigation.

We have, as yet, no evidence for the participation of the nickel atom in these rearrangements, but a preliminary Hückel M.O. calculation (we thank Dr. M. R. Willis and Mr. M. A. J. Wilks for this) for the metal-free macrocycle, indicates that such a thermal reaction could be concerted as the highest occupied molecular orbital would have the correct symmetry for the observed rearrangement. The order of the sigmatropic rearrangement[3] in these macrocycles is not obvious, but they may be regarded as 1,17 shifts [*cf.*, (II)] if the two cross-conjugated double bonds are disregarded.

Another example of this type of rearrangement has been observed with the nickel 1,19-diethoxycarbonyltetradehydrocorrin chloride (V; X = Cl).[4] Thermal rearrangement in chlorobenzene at 130° caused the loss of one ester group and rearrangement of the other to give (VI). This appears to be the first example of the sigmatropic rearrangement of an ester group. When the nitrate (V; X = NO_3) rather than the chloride, was treated similarly there was obtained in small quantity a second product in addition to (VI), in which one of the β-methyl groups of (VI) had been converted into a cyanide, presumably by nitrosation and dehydration of the resulting oxime ($CH_3 \rightarrow CH:NOH \rightarrow CN$). The nitrosation was presumably caused by a decomposition product of the nitrate anion.



(V)



(VI)

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