Reactions of Nickel 1,19-Dimethyltetradehydrocorrin Salts

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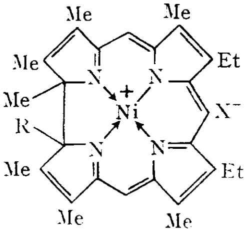
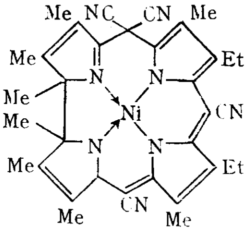
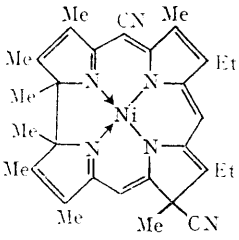
THE ready availability of nickel 1,19-dimethyltetradehydrocorrin salts[1] [*e.g.* (I; R = Me)] has led us to examine some of their chemical reactions. We have already established[2] that the salts of nickel 1-methyltetradehydrocorrins [*e.g.* (I; R = H)] readily exchange the *meso*-protons for deuterium in deuteriotrifluoroacetic acid, and so we anticipated that the action of electrophilic reagents on the salts (I; R = Me), would also lead to *meso*-substitution. Most of these reactions have now been found to involve only the C(5)*meso*-position, *e.g.* monobromo- (Br_2, 45%), monochloro- (acetyl chloride–stannic chloride, 60%, or Cl_2, 12%; under modified conditions the former reagent gave 36% 5-monochloro- and 6·7% 5,15-dichloro-derivatives), mononitro (cupric nitrate–acetic anhydride, 5%), monomethyl (methyl iodide–stannic chloride, 6·3%). The structures of these C(5) substitution products have been established on the basis of visible spectra (where large bathochromic shifts were observed), n.m.r. spectra and analyses.



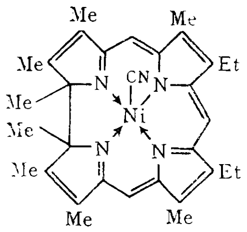
(I)



(II)



(III)



(IV)

The cationic species (I; R = Me) should also undergo ready reactions with nucleophiles and the action of cyanide has been investigated. When a methanolic solution of the nitrate of (I; R = Me) was heated under reflux with an excess of potassium cyanide, two neutral products, both containing several cyanide groups, were obtained. One of these, on treatment with acid, gave the 5,10,15-tricyano-1,19-dimethyltetradehydrocorrin salt, and the neutral precursor is tentatively formulated as the 5,5,10,15-tetracyano-compound (II). The second, and major (34%), neutral product from the cyanide reaction contained only two cyanide groups, and on treatment with hydrogen bromide in acetic acid it was converted almost quantitatively into the 5-cyano-derivative of the parent salt. On the basis of its n.m.r. spectrum, the precursor appeared to contain the additional cyanide group either at C(7) or at C(13) (as in III).

When the perchlorate of (I; R = Me) in methanol was treated similarly with potassium cyanide, the major product (80%) again was (III), (or the 7-cyano-isomer) but none of the tetracyano-derivative (II) was obtained. Instead a second neutral cyano-derivative was isolated, the visible spectrum of which exhibited no bathochromic shift compared with the starting material. This compound is assigned the pentaco-ordinate structure (IV) on the basis of analysis and its conversion by very small quantities of acid into the cyanide of the tetradehydrocorrin (I; R = Me, **X** = CN). The structures of all of the compounds mentioned above were assigned on the basis of analyses and interpretations of n.m.r. spectra.

(*Received, May 24th,* 1968; *Com.* 664.)

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[1] D. Dolphin, R. L. N. Harris, J. L. Huppatz, A. W. Johnson, and I. T. Kay, *J. Chem. Soc.* (*C*), **1966**, 30.

[2] D. A. Clarke, R. Grigg, R. L. N. Harris, A. W. Johnson, I. T. Kay, and K. W. Shelton, *J. Chem. Soc.* (*C*), **1967**, 1648.