

Substitution Reactions of Nickel 8,12-Diethyl-1,2,3,7,13,17,18,19-octamethyltetrahydrocorrins Nitrate

By A. HAMILTON and A. W. JOHNSON*

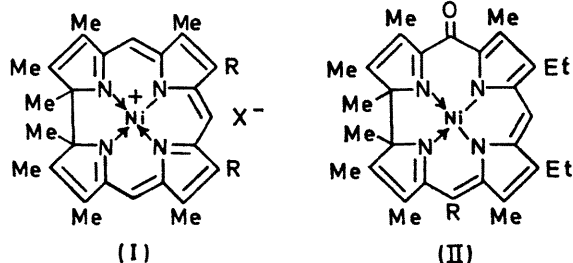
(School of Molecular Sciences, University of Sussex, Falmer, Brighton BN1 9QJ)

Summary Various substitution reactions of nickel 8,12-diethyl-1,2,3,7,13,17,18,19-octamethyltetrahydrocorrins nitrate show that the salt has a strong tendency for transformations into derivatives of the neutral 5-oxo-compound (II).

Our recent work on the substitution reactions of nickel 8,12-diethyl-1,2,3,7,13,17,18,19-octamethyltetrahydrocorrins nitrate necessitates that we amend and extend our earlier claims,¹ especially in view of a paper² on the nitration of nickel 1,2,3,7,8,12,13,17,18,19-decamethyltetrahydrocorrins perchlorate (I; R = Me; X = ClO₄). We now

parent oxo-compound (II; R = H)[†] is best obtained (60%) by the action of methyl-lithium in moist tetrahydrofuran on the salt (I; R = Et; X = NO₃) although somewhat lower yields are obtainable by more conventional alkaline reagents. The oxo-group is placed at C-5 rather than at C-10 because of the non-equivalence of the n.m.r. signals associated with the C-1 and C-19 methyl substituents (τ 9.33 and 9.4). The action of dilute aqueous sodium hydroxide on a chloroform solution of (I; R = Et; X = NO₃) gives an unstable blue chlorine-containing product [possibly (II; R = CHCl₂)] together with smaller amounts of the parent oxo-compound (II; R = H) and the 15-formyl-5-oxo-derivative (II; R = CHO).

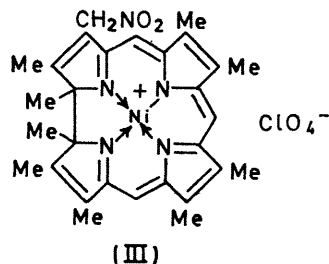
Reaction of (I; R = Et; X = NO₃) with methanolic potassium cyanide gives three neutral compounds. The most polar (18%) has been identified as the 15-cyano-5-oxo-compound (II; R = CN). The major product, the least polar fraction, is green and is converted into (II; R = CN) when an acetone solution is kept at room temperature for 2 days. On treatment with hydrogen bromide, this green product was converted quantitatively into the 5-cyano-derivative of the original salt, which also gave the keto-nitrile (II; R = CN) on treatment with alkaline hydrogen peroxide. The green compound is the free radical formed by oxidation of the intermediate neutral cyanide addition product of (I; R = Et; X = NO₃), and the e.s.r. spectrum ($g = 1.9993$; line width = 3.21 G) suggests that the odd electron is located on the ligand rather than on the metal. The remaining product of the cyanide addition is



report that these salts, particularly when they contain electron-attracting meso-substituents, are readily converted by bases, sometimes even by polar solvents, in presence of air into derivatives of the neutral oxo-compound (II). The

[†] All the compounds mentioned have been characterised by analyses and spectra.

also green and is the corresponding 5,15-dicyano-radical. With hydrogen bromide this radical gave the 5,15-dicyano-derivative of the original salt but this was readily reconverted into the radical during chromatography on alumina.



Bromination of (I; R = Et; X = NO₃) gave the blue perbromide of the 5,15-dibromo-derivative of the salt, but this was unstable and the bromine substituents proved to be very reactive. Lithium copper methyl⁸ gave the corresponding 5,15-dimethyl derivative, isolated (60%) as the perchlorate,⁴ and traces of acids caused rapid debromination of the nickel 5,15-dibromotetrahydrocorrins salt. This

acid-catalysed debromination recalls the behaviour of the bromo-2,3-dihydro-1*H*-1,4-diazepinium salts.⁵ Reaction of the dibromo-salt with alkaline hydrogen peroxide gave the oxo-compound (II; R = H) although preliminary debromination may well have occurred in this case also. In the nitration experiments we used copper nitrate in acetic anhydride at room temperature and obtained a product (80%) which was very reactive and apparently mainly the 5-nitro-derivative of (I; R = Et; X = NO₃). Attempts to purify this material gave a mixture of the 15-nitro-5-oxo-derivative (90%) (II; R = NO₂) together with the 10,15-dinitro-5-oxo-derivative (10%). Melenteva *et al.*² used fuming nitric acid for the nitration of (I; R = Me; X = ClO₄) and under various conditions claimed to isolate the 5-mononitro, both dinitro-isomers, and the 5,10,15-trinitro derivative of the salt, as well as a compound claimed to be the 3-nitromethyl derivative (III) when fuming nitric acid in acetic acid was used. The use of these experimental conditions with (I; R = Et; X = NO₃) has resulted in the formation of a product which was transformed by water to the same 10,15-dinitro-5-oxo-derivative as we had obtained earlier.

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