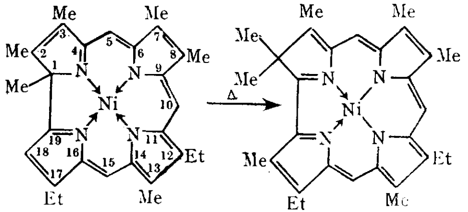
The Thermal Rearrangement of Nickel 1,19-Disubstituted Tetradehydrocorrin Salts

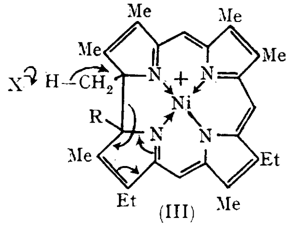
By R. GRIGG, A. W. JOHNSON,* K. RICHARDSON, and K. W. SHELTON

(*Department of Chemistry, University of Nottingham, University Park, Nottingham,* NG7 2RD)

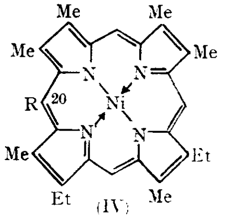
WE have shown previously[1] that the neutral nickel 2,3,7,8,12,13,17,18-octa-alkyl-1-methyltetradehydrocorrins[2] (I) rearrange to nickel 2,3,7,8,12,13,-17,18-octa-alkyl-2-methylcorroles (II) when they are heated in refluxing *o*-dichlorobenzene. Similar treatment of the nickel 19-substituted 1-methyltetradehydrocorrin salts[1,3] (III) leads to a different type of reaction and yields nickel porphins (IV). These have been found to be of two types, *meso*-monoalkyl (IV; R = alkyl) and *meso*-unsubstituted (IV; R = H), and the nature of the product has been shown to depend on the anion of the original salt. In both cases the carbon of the original C(1) methyl group becomes the C(20) *meso*-carbon of the porphin with loss of two or all three of its hydrogen atoms. The nickel *meso*-unsubstituted porphins were obtained by thermolysis of any of the salts of (III) except perchlorates which gave nickel porphins with the original tetradehydrocorrin C(19) alkyl group now present as a porphin C(20) *meso*-substituent (IV; R = alkyl) with no rearrangement of the migrating alkyl group (R = Me, Et, Pr^n, Bu^n, n-C_5H_{11}, allyl, $\cdot CH_2\cdot CH_2\cdot CO_2Et$). The allyl group however appeared as propenyl in the final product. The rearrangements of the perchlorates were markedly slower than those of the other salts and they tended to give mixed products. The initial step in these rearrangement reactions is considered to be a Hofmann-type elimination with the anion acting as base, and involving the C(1) methyl rather than the C(19) alkyl group, as is usual with this type of reaction (III; arrows). This leads to the fission of the macrocycle and the formation of the neutral nickel complex of the 1-methylene-1,19-dideoxybilatriene-*abc* (V). Some experimental support for this view has come from a study of the thermolysis of nickel 19-benzyl-1-methyltetradehydrocorrin bromides which yield the corresponding neutral, stable nickel 19-benzylidene-1,19-dideoxy-1-methylbilatrienes-*abc* [*e.g.* (VI)] after being heated in *o*-dichlorobenzene for 30 min. It is known[4] that Hofmann eliminations will involve benzyl rather than a methyl group. The formation



(I) (II)



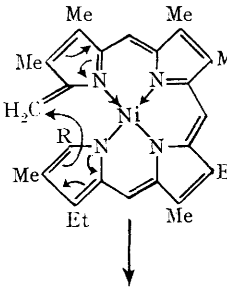
(III)



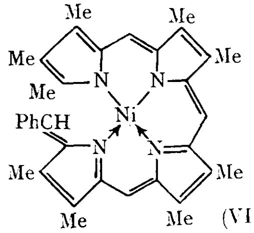
(IV)

of porphins from the 1,19-dideoxy-19-methylenebilatrienes-*abc* (V) is believed to involve intermediates (VII) but the details of the later stages of the reaction are still under investigation, as are the reasons for the unique behaviour of the perchlorates which contrasts sharply with that of other anions (nitrate, chloride, iodide, fluoride). In the case of a 1,19-dimethyltetradehydrocorrin iodide, where a methyl group was eliminated, it has been shown by mass spectral analysis of the volatile products, to be expelled as methyl iodide, *i.e.* implicating the anion once more in a late stage of the rearrangement reactions.

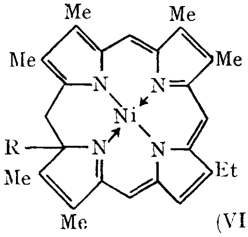
Exceptions to the above generalisations include nickel 1,2,3,7,8,12,13,17,18,19-decamethyltetradehydrocorrin chloride which, when heated, has been found to give the corresponding nickel *meso*-methylporphin in the form of its oxide (VIII), and the nickel 1,19-diethoxycarbonyltetradehydrocorrin nitrate and chloride which gave derivatives of corrole which we have described previously.[1]



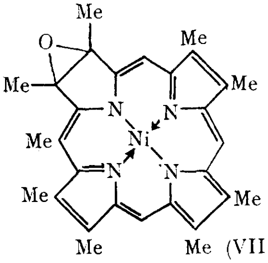
(V)



(VI)



(VII)



(VIII)

(*Received, May 24th,* 1968; *Com.* 665.)

---

[1] R. Grigg, A. W. Johnson and K. W. Shelton, *J. Chem. Soc.* (*C*), 1968, 1291; R. Grigg, A. W. Johnson, K. Richardson, and K. W. Shelton, *Chem. Comm.*, 1967, 1192.

[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.

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

[4] A. C. Cope, N. A. Le Bel, H.-H. Lee, and W. R. Moore, *J. Amer. Chem. Soc.*, 1957, **79**, 4720.