# *N*-Alkylation of Porphins and Related Macrocycles

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*Summary* The *N*-alkylation of octaethylporphyrin and related macrocycles is reported and the thermal reactions of these *N*-alkylated macrocycles and their metal complexes are described.

MONO-*N*-ALKYLATED PORPHINS have been known for some time[1,2] and their structures were confirmed by n.m.r. studies.[3] However, during the preparation of *N*-methylaetioporphyrin a second product formulated as an aetioporphyrin methiodide of uncertain structure was obtained.[1] We have prepared the analogous compound from octaethylporphyrin and formulate the product as the *NN'*-dimethylporphin iodide (I). The n.m.r. spectrum ($CDCl_3$) exhibited a six-proton singlet at $\tau$ 15·75 and the meso-protons occurred at $\tau$ − 0·40(S,2H), −0·35(S,1H) and −0·20(S,1H) whereas if methylation had occurred on opposite rings (*i.e.* II) the meso-protons should give rise to two 2H singlets, assuming the proton on nitrogen is not fixed but shared between the two remaining nitrogen atoms.[4] Evidence for the *trans*-arrangement of the two *N*-methyl groups comes from optical resolution studies of the D-camphor-10-sulphonate salt in which a specific rotation of *ca.* +200° was recorded after two recrystallisations from $CH_2Cl_2$–$Et_2O$.† Heating the dimethylporphin iodide (I) at 233—238° gives the *N*-methylporphin and octaethylporphyrin in varying amounts, whereas the zinc complex (III; M = Zn), in which the *N*-methyl group occurs at $\tau$ 16·05 in the n.m.r. spectrum, reverts to the zinc porphin at temperatures greater than 230°. The palladium complex (III; M = Pd) has also been prepared.

Alkylation of corroles [*e.g.* (IV; R = H) with methyl iodide and potassium carbonate gives separable mixtures

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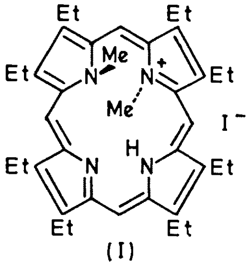
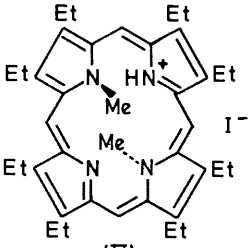
† The highly coloured nature of the macrocycles precluded accurate measurements. The macrocycle concentration was the same in all measurements and an increase of rotation of *ca.* 100° occurred on recrystallisation.

of isomeric *N*-methylcorroles[5] (IV; R = Me) and (V; R = Me). The demonstration that methylation of copper corrole anion gives an *N*-methyl copper corrole[6] prompted the preparation and study of the isomeric *N*-alkyl- and -allyl-corroles (IV and V; R = Me, Et, $\cdot CH_2\cdot CH{:}CH_2$, $CH_2\cdot CH{:}CMe_2$). The *N*-alkylcorroles (IV and V) did not form nickel complexes, and zinc formed only unstable complexes, but copper and palladium complexes could be prepared in high yield. [*e.g.* (VI; M = Cu, R = Et) (92%); (M = Pd, R = Me) (73%); (VII; M = Cu R = Et) (69%)]. Thermal interconversion of the isomeric copper *N*-ethylcorroles (VI and VII;) M = Cu, R = Et) was investigated but (VI); M = Cu, R = Et) underwent cleavage to copper corrole at 180° whereas (VII; M = Cu, R = Et) decomposed under these conditions. In contrast the palladium derivative (VI; M = Pd; R = Me) rearranged to the palladium 3,3-dimethylcorrole (VIII; 24%) at 180° whereas (VII; M = Pd, R = Me) gave mainly decomposition products together with a small amount of metal-free *N*-methylcorrole (V; R = Me). The structure of (VIII) was assigned on the basis of the similarity of its u.v. and n.m.r. spectra to those of the related nickel 3,3-dialkylcorroles[7] and position labelling in related palladium 3,3-dialkylcorroles using ethyl marker groups. Protonation of the palladium 3,3-dialkylcorroles with trifluoroacetic acid occurs at C-17 as in the corresponding nickel 3,3-dialkylcorroles.[7] Further alkylation of either (IV; R = Me) or (V; R = Me) using methyl iodide (sealed tube; 100°) gave an *NN'*-dimethylcorrole whose n.m.r. spectrum contained resonances due to meso-protons at τ 0·2(S,1H) 0·25(S,1H), and 0·55(S,1H). The *N*-methyl signals occurred at τ 12·5(S,3H) and 13·1(S,3H). The method of preparation limits the possible structures to (IX; $R^1$ = H, $R^2$ = Me or $R^1$ = Me, $R^2$ = H). The related macrocycle (X)[8] reacts with methyl or ethyl iodide to give either the mono *N*-alkyl derivative [XI; $R^1$ = Me (56%) or $R^1$ = Et (45%), $R^2$ = H] or, under more forcing conditions the *NN'*-dialkyl compound [XI; $R^1$ = $R^2$ = Me (81%) or Et (94%)]. As expected for alkyl groups at the centre of an aromatic macrocycle, the *N*-alkyl groups are strongly shielded in the n.m.r. spectra [*e.g.* n.m.r. spectrum ($CDCl_3$) of (XI; $R^1$ = $R^2$ = Me) exhibits signals due to the meso-protons at τ −0·31(S,2H) and 0·05(S,1H), and at τ 15·5(S,6H) for the *N*-methyl groups]. The *trans*-disposition of the *N*-alkyl groups in the *NN'*-dialkyl derivatives was evidenced by partial resolution of (XI; $R^1$ = $R^2$ = Et) as its D-camphorsulphonate which had a specific rotation of *ca.* + 200°† after two recrystallisations from acetone.



(I)



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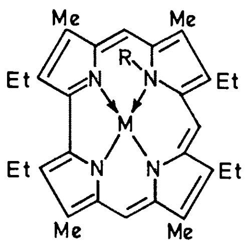
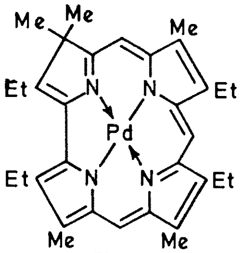


(VII)



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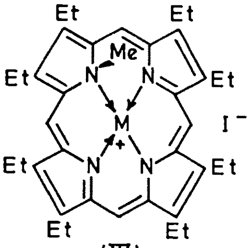
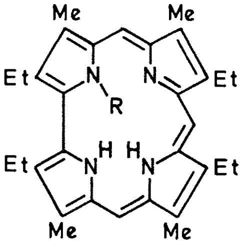
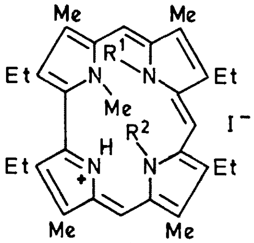


(III)



(IV)



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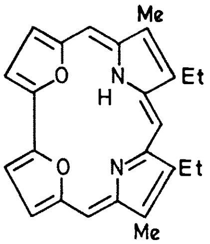
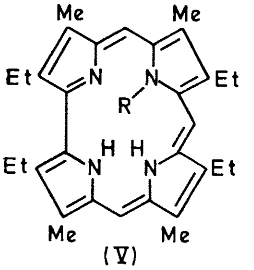
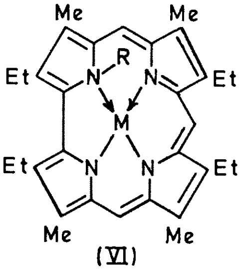


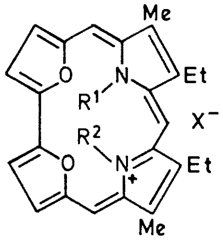
(X)



(V)



(VI)



(XI)

The thermal isomerisation of *N*-substituted pyrroles[9] prompted study of the thermal stability of the *N*-alkylcorroles but (IV; R = Me or Et) and (V; R = Me or Et) were unchanged after 12 hr. at 256° (boiling 1-chloronaphthalene). However, heating the *N*-allylcorrole (V; R = $CH_2\cdot CH{:}CH_2$) for 8 hr. at 110° (toluene) gave the isomeric *N*-allylcorrole (IV; R = $CH_2\cdot CH{:}CH_2$, 24%) together with corrole (V; R = H, 29%) whereas (IV; R = $CH_2\cdot CH{:}CH_2$) was unchanged under these conditions. When (V; R = $CH_2\cdot CH{:}CH_2$) was heated for 8 hr. at 110° in cumene the yield of (IV; R = $CH_2\cdot CH{:}CH_2$) fell to 10% and less corrole (V; R = H, 16%) was obtained, suggesting a radical process.‡ The *N*-dimethylallylcorrole (V; R = $CH_2{\cdot}CH{:}CMe_2$) in boiling toluene underwent isomerisation, without inversion of the dimethylallyl group, to (IV; R = $CH_2{\cdot}CH{:}CMe_2$, 16%) together with cleavage (V; R = H, 41%), supporting this view.

The mass spectra of the macrocycles (I) and (XI; $R^1 = R^2$ = Et, X = Br) were unusual in that instead of the expected parent ion at *m/e* *P* − HX (I; X = I; XI; X = Br) the parent ion occurred at *m/e* (*P* − HX) + 2. The macrocycles (X) and (XI; $R^1$ = H, $R^2$ = Et, X = Br) did not show this effect. These unexpected parent ions, presumably resulting from thermal reactions on the probe tip, may be related to the enhanced basicity of the *N*-alkylated macrocycles. The salts (I) and (XI; $R^1$ = H, $R^2$ = Et and $R^1 = R^2$ = Et) required methanol as eluant on an alumina column (Spence H) when they eluted unchanged.

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‡ The geometry of the participating orbitals precludes a concerted sigmatropic process unless the nitrogen atom bearing the allyl group undergoes a change in hybridisation from $sp^2$ to $sp^3$.

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