Reaction of Zinc Tetraphenylporphyrin Cation Radical Perchlorate with Pyridine

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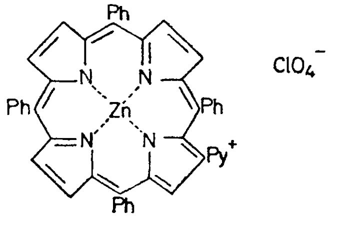
Summary Reaction occurs between zinc tetraphenylporphyrin cation radical $[Zn(TPP)^{\cdot+}ClO_4^-]$ and pyridine in acetonitrile solution and a pyridinium substituent enters a pyrrolic position of the porphyrin ring.

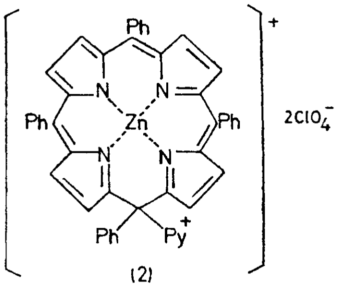
NUMEROUS examples of the reactions of aromatic and hetero-aromatic cation radicals with nucleophiles are now known.[1,2] In contrast, it has been generally accepted for some time that the π-cation radicals of metalloporphyrins are stable toward reaction with nucleophiles.[3] Only recently has this position been questioned. Barnett and Smith[4] have shown that oxidation of some metalloporphyrins by iodine followed by addition of nitrite ion, and oxidation by silver ion in the presence of nitrite ion, led to 'nitration' of the metalloporphyrins. The reactions were interpreted as being between the π-cation radicals and nitrite ion, in analogy with the reactions of aromatic cation radicals.[5] We have found that zinc(II) tetraphenylporphyrin cation radical perchlorate $[Zn(TPP)^{\cdot+}ClO_4^-]$ reacts readily with a number of nucleophiles and report here as an example the reaction with pyridine.

Tetraphenylporphyrin (TPP), purified as described by Smith,[6] had spectroscopic properties agreeing well with those in the literature.[7] Zn(TPP) was prepared in the usual way,[8] using zinc acetate. Crystalline $Zn(TPP)^{\cdot+}ClO_4^-$ was prepared by oxidation of Zn(TPP) with I_2–$AgClO_4$ in CH_2Cl_2. After filtration, the $Zn(TPP)^{\cdot+}ClO_4^-$ was precipitated with light petroleum and was purified by reprecipitation. Iodimetric assay gave 85—90% cation radical content in several preparations. The nature of the non-cation radical component is not known since work up of the iodimetric assay solutions showed only Zn(TPP) to be present by t.l.c. and visible spectroscopy.

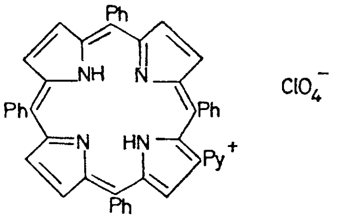
Addition of pyridine (1 ml) to Zn(TPP)$^{\cdot+}$ClO$_4^-$ (0·226 mmol active cation radical) in 20 ml of MeCN gave a red solution which very quickly turned green. The solvent was removed under reduced pressure after 30 min, the residue was dissolved in CH$_2$Cl$_2$, and the solvent was again removed after washing with water and drying. The residue was chromatographed on a column of alumina (activity III), giving (with CHCl$_3$) 61% of Zn(TPP) and (with Me$_2$CO) 33% of a greenish-blue solid. Elemental analysis (C, H, N, Cl) showed that the product was a mono perchlorate, and was in excellent agreement with structure (**1**) [λ_{max} (CH$_2$Cl$_2$) 594 ($10^{-4}\epsilon$ 1·28), 555 (1·67), 520sh (0·57), and 427 (27·0) nm; ν_{max} 1090 br cm^{-1} (ClO$_4^-$)]. The compound did not melt below 400 °C but appeared to decompose slowly during the heating. Analogous reaction of Zn(TPP)$^{\cdot+}$ClO$_4^-$ with C$_5$D$_5$N gave 65% of Zn(TPP) and 25% of [^{2}H$_5$]-(**1**) [λ_{max} (CH$_2$Cl$_2$) 594 ($10^{-4}\epsilon$ 1·14), 555 (1·56), 520sh (0·58), and 427 (24·0) nm].



(1)



(2)



(3)

The n.m.r. spectra of (**1**) and [^{2}H$_5$]-(**1**) (Varian model XL-100) are consistent with the structures assigned and will be given in detail in a full publication. The pyrrolic protons all appear downfield from those of the phenyl rings, demonstrating that the aromaticity of the porphyrin ring has not been interrupted by substitution at a *meso* position (structure **2**). It is evident, too, that had such substitution occurred, the product would have been a dication diperchlorate, which is also inconsistent with the elemental analysis.

To show that the pyridine unit in (**1**) is really substituted on the porphyrin ring and not complexed with the central zinc atom, the zinc was removed from both (**1**) and [^{2}H$_5$]-(**1**) by treatment with 70% HClO$_4$ in methanol. Work-up of the product from (**1**) gave the pyridinium perchlorate derivative of TPP (**3**) with satisfactory elemental analysis (C, H, N, Cl) and n.m.r. spectrum [λ_{max} (CH$_2$Cl$_2$) 655 ($10^{-4}\epsilon$ 1·14), 600 (0·746) 523 (1·73), and 420 (27·0) nm]. Work-up of the product from [^{2}H$_5$]-(**1**) gave [^{2}H$_5$]-(**3**), the n.m.r. spectrum of which was used in elucidating that of (**3**).

Although the product obtained is not an isoporphyrin (**2**), we have isolated from the C$_5$D$_5$N reaction a small amount (8 mg) of material, the absorption spectrum of which has the character of an isoporphyrin.[9] The exact structure of this compound has not yet been established.

It is evident that Zn(TPP)$^{\cdot+}$ClO$_4^-$ in solution reacts with pyridine (py), and the stoicheiometry of the reaction, in spite of the non-quantitative yields, seems to be of the usual kind[2] as shown in equation (1).

$$2\ \text{Zn(TPP)}^{\cdot+}\text{ClO}_4^- + \text{Py} \rightarrow \text{Zn(TPP)} + (\mathbf{1}) + \text{HClO}_4 \qquad (1)$$

Our result fortifies the earlier finding[4] that solutions of metalloporphyrin π-cation radicals are not inert toward nucleophiles. Whether or not the cation radical is involved in direct reaction with the pyridine will be discussed later.

We have carried out analogous reactions of Zn(TPP)$^{\cdot+}$ClO$_4^-$ with NO$_2^-$, SCN$^-$, MeOH, Ph$_3$P, and Ph$_3$As. In each case, reaction occurred readily, and in all cases the product appears to contain the nucleophile at a pyrrole carbon atom, except in the case of MeOH from which the methoxyisoporphyrin perchlorate, described earlier by Dolphin, *et al.*[9] was obtained. Details of these reactions will be reported elsewhere.

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