Synthetic 2- and 4-Monoacetyldeuteroporphyrin IX

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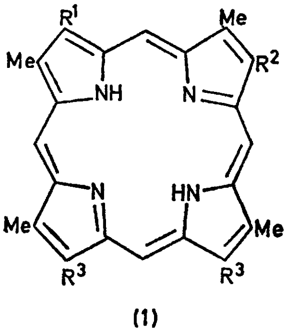
Summary The synthesis of 2- and 4-monoacetyldeuteroporphyrin IX dimethyl ester has been achieved and as a result the structural assignments given to the two isomers obtained by acetylation of deuteroporphyrin should be revised.

As part of an investigation which examined the potential of the copper acetate–pyridine cyclisation[1] of bilenes and biladienes as a useful porphyrin synthesis the preparation of pemptoporphyrin dimethyl ester (**1a**) was undertaken. For this purpose 4-acetyldeuteroporphyrin dimethyl ester (**1b**) was prepared by the condensation of (**2a**) with the imine salt (**2b**) to give the intermediate bilene which was not isolated but cyclised with copper acetate–pyridine[1] to give the desired porphyrin (**1b**) in 15% yield. Russian workers[2] have reported the successful preparation of at least one porphyrin in good yield by the condensation of an α-formyl-α′-methyldipyrrylmethane and an αα′-unsubstituded dipyrrylmethane followed by oxidative cyclisation with copper acetate. We found that this type of procedure yielded large amounts of *meso*-pyrrylporphyrin presumably derived from attack of two moles of the formylmethane upon the second reactant to give an intermediate hexapyrrene.[3] However the use of imine salts of the type (**2b**)† afforded protection against condensation with the formylmethane at one end of the molecule and thus avoided the formation of *meso*-pyrrylporphyrins as by-products.



(1)

	R^1	R^2	R^3
a	H	$CH{=}CH_2$	$[CH_2]_2\cdot CO_2Me$
b	H	Ac	$[CH_2]_2\cdot CO_2Me$
c	Ac	H	$[CH_2]_2\cdot CO_2Me$

The melting point of (**1b**) prepared as above was 212° which agreed with the value reported by Brockmann *et al.*[5] for the compound which these workers suggested was the 2-acetyl isomer. This discrepancy led us to attempt the synthesis of 2-acetyldeuteroporphyrin dimethyl ester (**1c**) which was completed by the cyclisation of the intermediate

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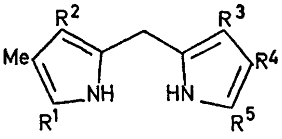
† This was prepared by decarboxylation of the dicarboxylic acid (**2c**) in *NN*-dimethylformamide under reflux followed by treatment with 1 mol of benzoyl chloride.[4]

bilene derived from (**2b**) and (**2d**) although in this case pyridine proved not to be such a useful solvent. Better yields (12%) of (**1c**) were obtained when the intermediate bilene was cyclised with copper acetate in acetic acid: methanol (2:1), the solvent used by Rumyantseva *et al.*[2] The 2-acetyl-derivative (**1c**) had a m.p. 240° identical with the value recorded by the German workers for the compound assigned by them as the 4-acetyl isomer.



(2)

	R^1	R^2	R^3	R^4	R^5
a	CHO	H	Me	Ac	Me
b	$\mathrm{Me_2\overset{+}{N}{=}CH}$	$\mathrm{[CH_2]_2{\cdot}CO_2Me}$	$\mathrm{[CH_2]_2{\cdot}CO_2Me}$	Me	H
c	$\mathrm{CO_2H}$	$\mathrm{[CH_2]_2{\cdot}CO_2Me}$	$\mathrm{[CH_2]_2{\cdot}CO_2Me}$	Me	$\mathrm{CO_2H}$
d	Me	Ac	Me	H	CHO

Our synthetic 4-acetyldeuteroporphyrin has been converted into pemptoporphyrin dimethyl ester (**1a**) by reduction and dehydration following published methods.[1,6] This vinyl-porphyrin has been shown to be identical with a sample prepared independently by Professor Kenner and his colleagues[7] whom we thank for their help in providing material. The preparation of pemptoporphyrin from our synthetic 4-acetyldeuteroporphyrin is further confirmation of its structure.

In view of our results we suggest that the structural assignments given to the monoacetyldeuteroporphyrins derived by direct electrophilic substitution of deuteroporphyrin be reversed.[5]

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