Porphyrins from Electronegatively Substituted Bilenes

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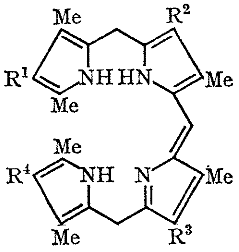
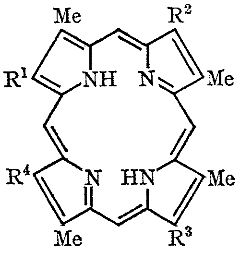
Summary Porphyrins bearing electronegative groups have been obtained by the cyclisation of appropriately substituted 1,19-dimethyl-1,19-dideoxybilenes using cupric salts in pyridine solution.

THE successful preparation of porphyrins by the cyclisation of 1,19-dimethyl-1,19-dideoxybilene-*b* or biladiene-*ac* salts which bear alkyl substituents has been reported by Johnson and his colleagues.[1] A recent communication[2] from the same laboratory records an important improvement to this procedure. However, an attempt[3] to extend this method to systems involving electronegative groups resulted in the porphyrin being obtained in prohibitively low yields. We now report a procedure by which the cyclisation of electronegatively substituted bilenes and biladienes can be achieved giving the porphyrin in good yields.

From another project we had on hand a range of 5-formyl-5′-methyldipyrrylmethanes which by condensation in an acidic medium with a 5-carboxy-5′-methyldipyrrylmethane provided a series of 1,19-dimethyl-1,19-dideoxybilene-*b* salts bearing a variety of substituents (Ia—d). These bilene salts were cyclised in pyridine solution by stirring with an excess of copper(II) acetate for 2 hr. at room temperature, followed by a similar period at 60°. In this way the porphyrins (IIa—d) were obtained in 20% yield after removal of the metal from the intermediate copper complex. A similar cyclisation of the biladiene (III) gave the porphyrin (IVa) in 30% yield but it is too early to say whether this increased yield is significant.



(I)

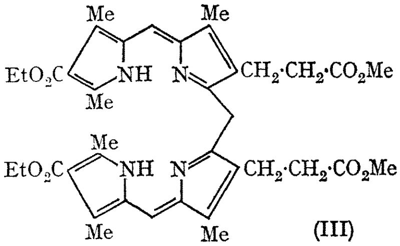


(II)

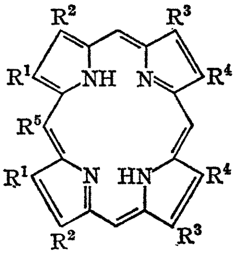
	R^1	R^2	R^3	R^4
a	COMe	Me	Me	COMe
b	COMe	Me	Et	COMe
c	COMe	Me	Me	CO_2Et
d	COMe	Br	Me	CO_2Et

TABLE

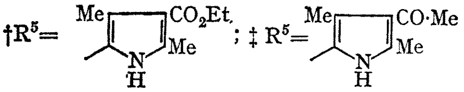
Porphyrin	m.p.	*Electronic spectra* [$\lambda_{max.}$ ($CHCl_3$) nm. (log ϵ)]
(IIa)	>350°	423(5·18), 516(4·06), 553(3·96), 587(3·83), 640(3·70)
(IIb)	>350°	422(5·21), 515(4·06), 553(3·96), 586(3·79), 640(3·68)
(IIc)	324—327°	419(5·27), 513(4·11), 550(3·98), 585(3·85), 638(3·72)
(IId)	283—285°	421(5·32), 515(4·14), 551(4·06), 584(3·87), 639(3·58)
(IVa)	283—285°	418(5·32), 510(4·17), 544(3·97), 580(3·83), 634(3·72)
(IVb)	192—194°	402(5·25), 501(4·19), 533(3·66), 573(3·75), 623(3·26)
(IVc)	>350°	407(5·15), 505(4·10), 537(3·83), 572(3·77), 624(3·54)

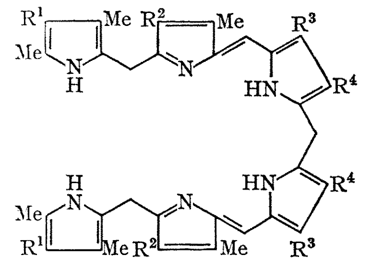


(III)



		R^1	R^2	R^3	R^4	R^5
(IV)	a	CO_2Et	Me	Me	$[CH_2]_2 \cdot CO_2Me$	H
	b	$[CH_2]_2 \cdot CO_2Me$	Me	H	H	†
	c	Me	Me	Me	$[CH_2]_2 \cdot CO_2Me$	‡





		R^1	R^2	R^3	R^4
(V)	a	CO_2Et	$[CH_2]_2 \cdot CO_2Me$	H	H
	b	COMe	Me	Me	$[CH_2]_2 \cdot CO_2Me$

In another series of experiments the hexapyrrenes (Va; Vb) were prepared by the condensation of a 5,5′-diformyldipyrrylmethane with 2 moles of a 5-carboxy-5′-methyldipyrrylmethane. Similar treatment of these hexapyrrenes with cupric acetate in pyridine gave the *meso*-pyrrylporphyrins (IVb; IVc) in 30% yield. The structure of this novel class of porphyrin followed directly from their mass spectra which showed the appropriate molecular ion and from their n.m.r. spectra which contained only three methine protons and possessed the appropriate resonances for the *meso*-pyrryl substituent at higher field than the strongly deshielded substituents of the porphyrin ring proper. For example, porphyrin (IVb) in $CDCl_3$ showed resonances at δ 9·61, 9·23 (2H, 1H, methines), 8·60 (4H, m, aromatic protons), 7·8 (1H, pyrrolic NH), 4·1 (2H, q, OCH_2CH_3), 3·50 (6H, OCH_3), 3·10 (6H, porphyrin ring CH_3), 2·5, 2·0 (4H, 4H, m, $\cdot CH_2\cdot CH_2\cdot$), 2·03, 1·42 (3H, 3H, pyrrolic CH_3), 1·23 (3H, t, OCH_2CH_3), $-3{\cdot}9$ (2H, porphyrin NH). Obviously there is a significant interaction between the *meso*-pyrryl substituents and the propionic acid groups on the porphyrin ring since the resonances due to the methylenes of the propionic acid, as well as one methyl of the pyrryl substituent and the pyrrolic NH are all found at much higher field than is normal. Whether this is due to steric effects or to field effects arising from the presence of two aromatic systems is not clear.

The success of this procedure greatly extends the scope of porphyrin syntheses that can be achieved from the bilenes and biladienes. The mildness of the method together with the fact that unsymmetrical porphyrins bearing a wide range of alkyl and electronegative substituents can be prepared makes this an attractive route for the preparation of some naturally occurring porphyrins having labile side-chains.

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