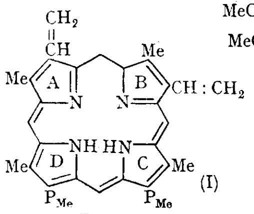
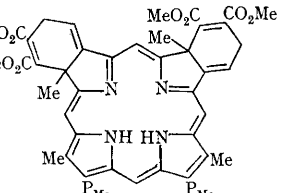
Diels–Alder Additions to Protoporphyrin IX Dimethyl Ester

By R. GRIGG, A. W. JOHNSON,* and A. SWEENEY
(*Department of Organic Chemistry, University of Nottingham, Nottingham* NG7 2RD)

ADDITIONS to the β double bonds of porphins, which result in the formation of *gem*-β-substituents are of interest because of the relation between the porphin and vitamin B_{12} structures. Certain of these additions have been described in the literature,[1] but the reactions are not generally applicable. Related to these addition reactions is the acid rearrangement of the hydroxylation products of porphins, *e.g.* 2,3-dialkyl-2,3-dihydroxychlorins to 2,2-dialkyl-3-oxochlorins.[2] We report that protoporphyrin IX dimethyl ester (I) undergoes Diels–Alder additions with two equivalents of an activated dienophile, such as dimethyl acetylenedicarboxylate or tetracyanoethylene, to form adducts (II and III; 40 and 56% respectively) where both the exocyclic double bonds and the two cross-conjugated β-double bonds of the protoporphyrin ester constitute the diene systems. The products still retain the aromatic 18π-electron system and are α-dihydrochlorin derivatives.[3] Analyses of the adducts are in agreement with the suggested structures and further work on reactions of the products is in progress.

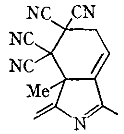


(I)



(II)

$P_{Me} = \cdot CH_2\cdot CH_2\cdot CO_2Me$



(III; Rings A and B, rings C and D as in I and II)

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