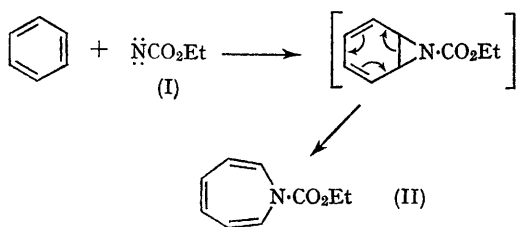


The Reaction of Ethoxycarbonylnitrene with Porphyrins. A Ring Expansion-Contraction Reaction of the Porphyrin Ring

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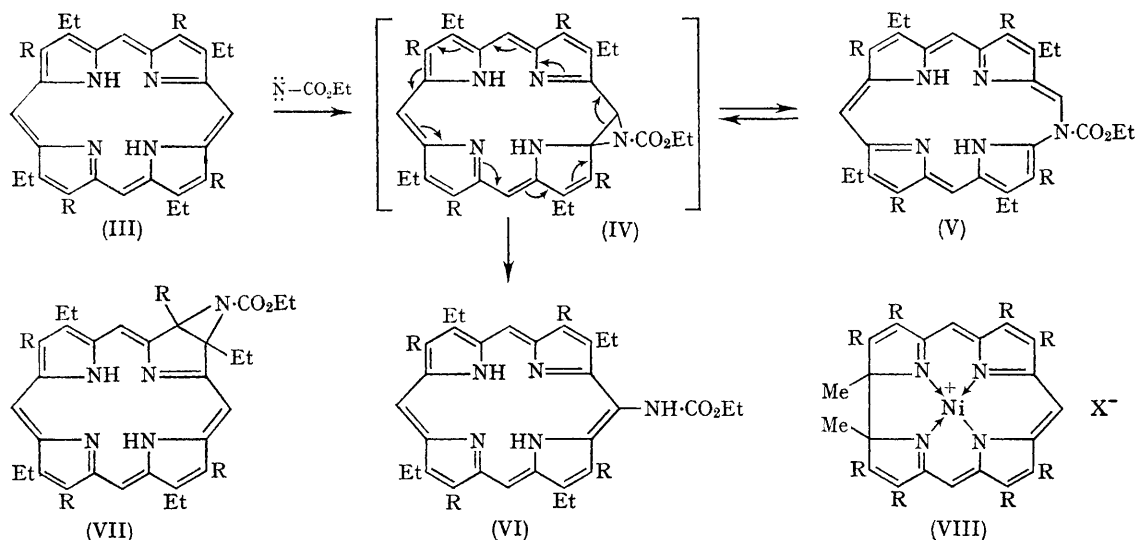
THE great interest in the *meso*-reactivity of porphyrins stems from both the intrinsic interest of the aromatic macrocycle and the relationship of *meso*-reactivity to the catabolism of heme, the blood pigment. A number of electrophilic substitution reactions at the *meso*-position have been investigated¹⁻⁴ but no reactions with electron-deficient species have been reported. The reaction of benzene with ethoxycarbonylnitrene (I) to give the azepine (II)⁵ suggested a possible method of porphyrin ring expansion providing reaction occurred at the *meso*-position.



We have examined the reaction of ethoxycarbonylnitrene^{5b} with both porphyrins and metalloporphyrins and these reactions are conveniently carried out at room temperature in methylene

chloride. The reaction of ethoxycarbonylnitrene with the porphyrins (III; R = Me, Et) followed by careful isolation of the products without the application of heat gave compounds formulated as ring-expanded porphyrins (V; R = Me, Et) on the basis of their spectral and chemical properties.

The n.m.r. of the products (V; R = Me, Et) exhibit four different methine protons at τ 2-3.2 (60 Mc./sec. in CCl_4) which militates against a chlorin structure such as (VII) and the n.m.r. together with the presence of a Soret band [e.g., (V; R = Et) λ_{max} (Et_2O) 404, 610, and 655 $m\mu$, ϵ_{max} 69,000, 11,000 and 12,800, respectively, λ_{infl} 530 and 570 $m\mu$, ϵ_{infl} 4460 and 7580, respectively] indicates these compounds are not the valence tautomers (IV; R = Me, Et). The ring-expanded porphyrins (V; R = Me, Et) undergo a smooth ring contraction to the corresponding *meso*-substituted porphyrins (VI; R = Me, Et) in chloroform solution or by heating the solid to ca. 160°. This ring contraction presumably proceeding *via* the valence tautomer (IV). A similar, though less efficient, ring contraction of the azepine (II) has been observed at 150°. The structures of the *meso*-substituted porphyrins (VI; R = Me or Et) are readily apparent from their spectral properties. Thus the visible spectra are of the



actio-type as observed for *meso*-acetamidoaetio-porphyrin I,² [*e.g.*, (VI; R = Et) λ_{max} (CHCl₃) 405, 504, 538, 574, and 628, ϵ_{max} 184,000, 15,200, 8760, 6830, and 4330, respectively]. The n.m.r. spectra clearly demonstrated the presence of only three *meso*-protons [*e.g.*, (VI; R = Et) τ 0.0, 1 proton singlet; τ -0.2, 2 proton singlet) and the infrared spectra confirm the presence of the urethane group [*e.g.*, (VI; R = Et) ν_{max} (KBr) 1735 cm.⁻¹].

The reactions of a number of porphyrin-metal complexes (Zn^{II}, Cu^{II}, Ni^{II}, Co^{III}) of (III; R = Me)

with ethoxycarbonylnitrene have also been studied and *meso*-substituted products corresponding to (VI) isolated in the case of the zinc and copper complexes. No reaction was observed with the nickel complex but this may have been largely due to solubility difficulties and is being reinvestigated with a more soluble nickel porphyrin. The deactivating effect of the positive charge in the Co^{III} porphyrin complex contrasts with the ready electrophilic substitution observed in 1,19-dimethyltetrahydrocorrin salts (VIII).⁶

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