

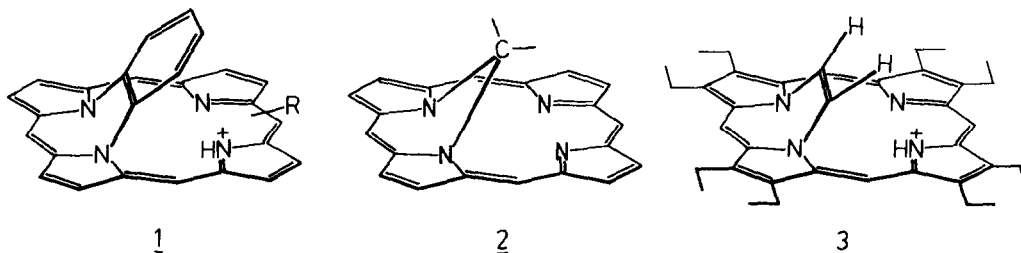
OXIDATIVE CYCLIZATION OF SUBSTITUTED N-VINYLPORPHYRIN COBALT COMPLEXES.  
SYNTHESIS OF N,N'-(1,2-VINYLDENE) AND N,N'-(1,2-PHENYLENE)PORPHYRINS.

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*Summary.* The oxidative cyclization of substituted N-vinylporphyrin cobalt complexes gave N,N'-1,2-vinylidene porphyrins. In the case of a cyclic fragment further dehydrogenation gave a product similar to the 1,2-phenylene bridged porphyrin obtained on inactivation of cytochrome P-450 by 1-aminobenzotriazole.

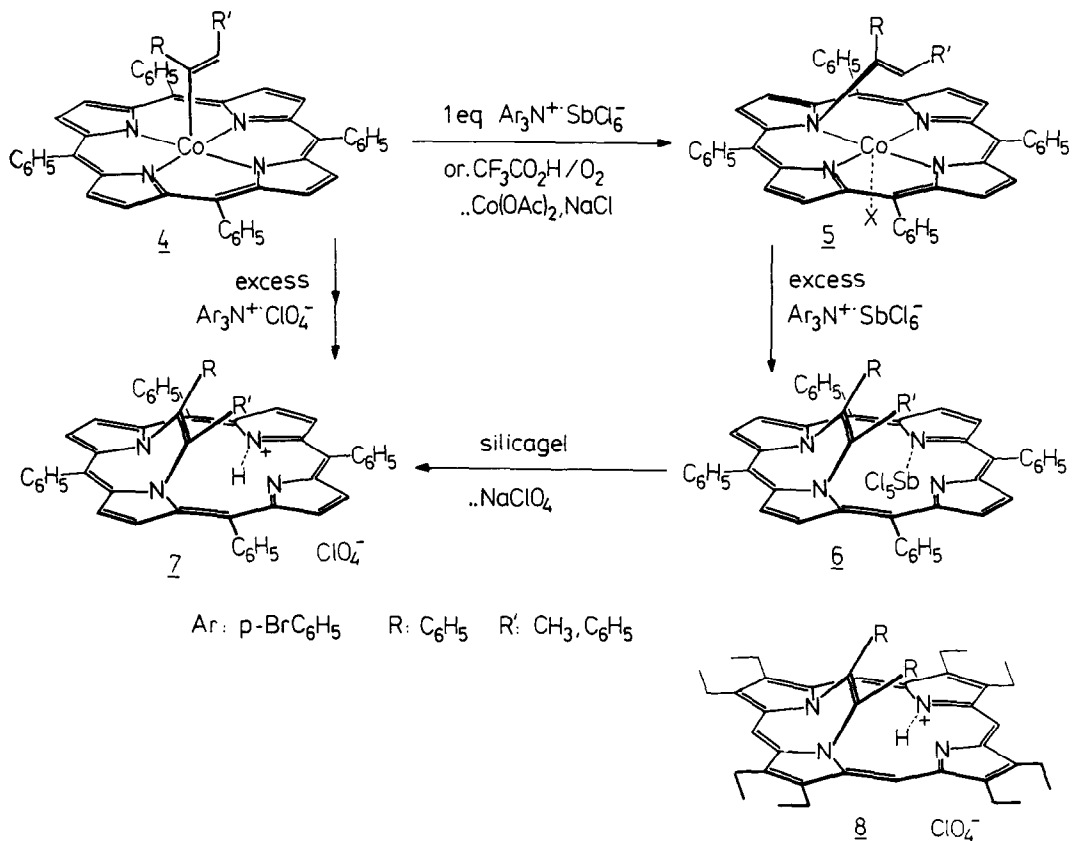
Porphyrins bridged between two adjacent nitrogen atoms remained laboratory curiosities until Ortiz de Montellano<sup>1</sup> demonstrated that the products of inactivation of cytochrome P-450 by 1-aminobenzotriazole had structure 1 (mixture of isomers), supposed to arise from the addition of benzyne over iron-protoporphyrin. Although several methods<sup>2,3,4</sup> are available to obtain a single-carbon bridged porphyrin (general structure 2) the only synthesis of a two-carbon bridge 3 was reported by Dolphin<sup>5</sup> and is an acid catalyzed enamine formation from a N-formylmethylporphyrin. In this article we report that the oxidative cyclization of substituted Cobalt N-vinylporphyrins gives N,N'-1,2-vinylideneporphyrins and opens a route to the synthesis of N,N'-1,2-phenyleneporphyrins, models of structure 1.



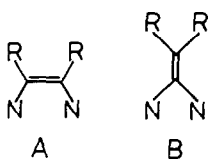
R: substituents of  
protoporphyrin

When submitted to one-electron oxidation alkyl, vinyl, styryl or arylcobalt (III)porphyrins<sup>6-9</sup> (as well as various R-iron(III)porphyrins<sup>10</sup>) rearrange to N-substituted porphyrins. Accordingly<sup>8,11</sup> we prepared chlorocobalt(II)-N-substituted tetraphenyl porphyrins 5 from 4. On further oxidation (excess  $(p\text{-BrC}_6\text{H}_4)_3\text{N}^+\text{SbCl}_6^-$ ) 5 cyclized to give bridged compounds 6. Chromatography (silicagel ;  $\text{CH}_2\text{Cl}_2$  + 3% AcOEt) gave pure 6 whereas

on standing on the column (or in the presence of acid) 6 transformed into salts 7 (eluted with  $\text{CH}_2\text{Cl}_2 + 5\% \text{ MeOH}$ ), crystallized as perchlorates (yields 20-35% from 4 to 7). One step conversion of 4 into 7 was also realized using an excess  $(p\text{-BrC}_6\text{H}_4)_3\text{N}^+\text{ClO}_4^-$ . The reaction was extended to the octaethylporphyrin (OEP) series (8) but failed when an unsubstituted vinyl or an  $\alpha$ -styryl group was attached to N.

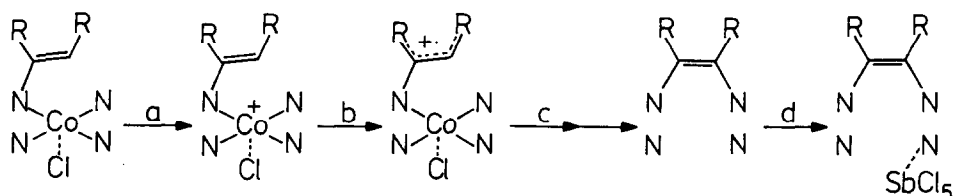


The n.m.r. spectra<sup>12</sup> of 6, 7, and 8 ( $\text{R}=\text{R}'=\text{C}_6\text{H}_5$ ) demonstrate the existence of a plane of symmetry: there must be a rapid exchange of proton or  $\text{SbCl}_5$  (if one assumes hexacoordination for Sb) between the two non-bridged N (we locate the  $\text{SbCl}_5$  group opposite to the bridge by analogy with the known one carbon bridged  $\text{PdBBr}_2$  complex<sup>3</sup>). Of particular interest are 1) the very large shielding of the bridge phenyl protons (ortho ca 2.6 ppm above coalescence<sup>12</sup>), 2) the fact that the spectra of 6 and 7 are almost superimposable, demonstrating that the effect of a proton or a  $\text{SbCl}_5$  group is similar. There remained the possibility of two isomeric structures (bridges A and B). A compound of type B was

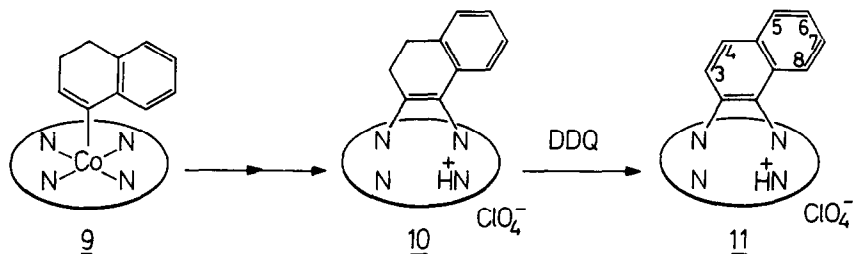


described by Mansuy<sup>4</sup> and showed somewhat different n.m.r. and visible spectra data.  $^{13}\text{C}$  labeled 7 ( $\text{R}=\text{R}'=\text{C}_6\text{H}_5$ , both bridge C identically labeled) showed only one enhanced quaternary  $^{13}\text{C}$  resonance in various solvents thus excluding any type B structure.

We propose the following mechanism for the cyclization reaction : a) oxidation of Co(II) to Co(III) (no reaction occurred in the absence of metal), b) electron transfer<sup>13</sup> from the olefinic group (this step should be favored by CH<sub>3</sub> or C<sub>6</sub>H<sub>5</sub> groups, explaining why simple vinyl or  $\alpha$ -styryl substituted porphyrins do not react, c) nucleophilic attack of a vicinal pyrrolic N followed by oxidation of the resulting radical, deprotonation and loss of cobalt, d) coordination of SbCl<sub>5</sub> (from the SbCl<sub>6</sub><sup>-</sup> counterion).



A bridging aromatic group was obtained when we followed the same sequence starting with 9 (from tetralone tosylhydrazone and a Co(III)porphyrin<sup>11</sup>; TPP series). The resulting dihydronaphthalene 10 was aromatized to 11<sup>14</sup> by heating with DDQ.



Although this synthesis of two-carbon bridged porphyrins does not pretend to be a model for the aminobenzotriazole - P450 reaction it is of importance to note that both reaction sequences occur under oxidative conditions. Extension of the reaction to the direct bridging of aromatic substituents is in progress.

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References and notes

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12. N.m.r. data for compound 7 ( $R=R'=C_6H_5$ ) ( $CDCl_3$ , 200 MHz, 310°K) : 9.22 and 9.17 (4H, AB, pyrrolic H), 8.82 and 8.78 (4H, AB, pyrrolic H), 8.4-7.0 (20H, several multiplets, meso-phenyl), 6.36 (2H, t, bridge p-H), 5.94 (4H, broad t, bridge m-H), 2.6 (4H, very broad, bridge o-H ; this signal splitted at 223°K to two still unresolved signal at 4.1 and 1.1 ppm. Coalescence occurred at ca 253°K,  $\Delta G_{TC}^\ddagger = 11 \text{ kcal M}^{-1}$ ). The methyl group of compound 7 ( $R=C_6H_5$ ,  $R'=CH_3$ ) gave a signal at -2.99 ppm. Visible spectrum (7,  $R=R'=C_6H_5$  ;  $CH_2Cl_2$ ):  $\lambda_{max} = 430, 554, 592, 640$  ( $\epsilon$  resp. 168000, 10000, 15200, 6200).
13. Oxidation of olefins by cobalt(III) proceeds via initial electron transfer. See for example : M. Hirano, K. Nakamura and T. Morimoto, J. Chem. Soc. Perkin II, 817-820 (1981) ; M. Hirano and T. Morimoto, J. Chem. Res. (S) 104, (M) 1069-1086 (1979).
14. N.m.r. data for compound 11 (TPP series) ( $CDCl_3$  ; 200 MHz) 9.2-8.8 (8H, m, pyrrolic H), 8.5-7.6 (20H, m, meso-phenyl), 6.79 and 6.53 (1+1H, 2t, H-6 + H-7), 6.12 (1H, d, H-5), 5.51 (1H, d, H-8), 4.91 (1H, d, H-4), 2.18 (1H, d, H-3). Visible spectrum ( $CH_2Cl_2$ ):  $\lambda_{max} = 436, 562, 600, 650$  ( $\epsilon$  resp. 99000, 7300, 10400, 6500).

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