SYNTHESES OF PYRROLES AND PORPHYRINS SUBSTITUTED WITH TRIFLUOROMETHYL GROUPS

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Pyrroles and porphyrins substituted with the CF_3 groups were prepared to obtain the heme replaceable with naturally occurring hemes of hemoproteins and heme enzymes. Firstly introduction of the CF_3 group reduces reduction potentials of those proteins and enzymes. Secondly site-specific trifluoromethylation of heme at peripheral four positions may provide information about interaction between apo-protein and prosthetic group by monitoring $^{19}\mathrm{F-NMR}$ spectroscopy.

Two CF $_3$ groups were introduced at the 2 and 4-positions of deuteroporphyrin-IX by photochemical reaction with CF $_3$ I and copper salt. However, this reaction resulted in concomitant formation of diiodo and monoiodo-monotrifluoromethyl derivatives as major products. Stepwise synthesis from two kinds of trifluoromethylpyrroles gave 1,1,1,3,3,3-hexafluoro-mesoporphyrin-IX. Successive reduction with B_2H_6 gave 3-hydroxyethyl-4-trifluoromethylpyrrole as a key compound for building the trifluoromethylated protoheme-IX in site-specific manner. Paramagnetic ^{19}F -NMR of met-heme and met-myoglobin reconstituted with new heme will be described by comparing diamagnetic signals of metalloporphyrins.