SYNTHESIS OF FLUORINE CONTAINING PYRROLES AND THEIR DERIVATIVES

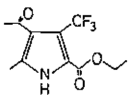
Hiroo Toi, Michihide Homma, Hiroyuki Onda, Katsuhiro Aoyagi,
Yasuhiro Aoyama and Hisanobu Ogoshi
Technological University of Nagaoka, 1603-1 Kamitomioka, Nagaoka, Niigata
949-54, Japan and Fukushima Technological College, Taira-kamiarakawa,Iwaki,
Fukushima 970, Japan

Pyrroles and porphyrins containing fluorine and perfluoroalkyl groups were prepared. These were designed for studying on controlling the redox potentials of porphyrin metal complexes and stabilyzing low oxidation state metal complexes, and for utilyzing as a probe in nmr study of metalloenzymes. Furthermore, fluorine containing pyrroles are interesting as analogues of bromine containing pyrroles which are found among physiologically active marine products.

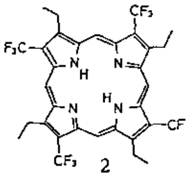
Pyrrole 1 was obtained in 31 % yield by modified Knorr method using gaseous $HNO_2/CF_3COOH/Zn$ instead of $NaNO_2/CH_3COOH/Zn$ system. Porphyrin 2 was given in c.a. 10 % overall yield from 1 with several steps and Cu-template method. Non-template method was unsuccessful. Porphyrin 3, iron complex of which can be incorporated in apo-hemoproteins, was also synthesized from 1 through dipyrrolemethanes and coupling at β,δ-meso positions.

pyrrole 4 was prepared in 25 % yield by photochemical reaction of pyrrolediazonium tetrafluoroborate salt. Converting 4 to 2-hydroxymethyl-3-fluoro-4-methylpyrrole-5-carboxylic acid followed by tetramerization in the presence of $K_3Fe(CN)_6$ yielded porphyrin 5.

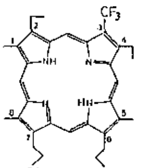
Electron defficiency of porphyrin 3 was indicated in the redox potentials. E_1 and E_2 of 3 are -850 and -1180 mv vs. SCE, respectively, showing 500-600 mv anodic shift compared with a normal etio type porphyrin. Same trends were obtained in the metal redox potentials of the metal complexes. The physicochemical properties of these compounds will be also reported.



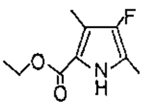
1



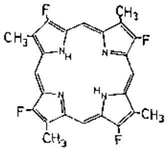
2



3



4



5