NEW TYPE OF IPSO-SUBSTITUTION IN PYRIDINE RING AND ITS APPLICATION FOR THE SYNTHESIS OF MACROCYCES CONTAINING BOTH OXA- AND THIA-BRIDGES

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Recently, we have prepared several new sulfur compounds containing pyridine ring and shown that for example, alkyl 2-pyridyl sulfoxides or 2,6-disulfinylated pyridine derivatives can be used as phase transfer catalysts. In this meeting, we wish to report the new type of ipso-substitution in the sulfoxides and sulfones containing pyridine ring with nucleophiles and its application for the synthsis of new type of macrocyclic compounds containing pyridine ring.

The synthesis of 2,6-pyridino macrocycles in which the bridging oxygen and sulfur directly attached to pyridine ring was carried out as shown in the following Scheme. Initially, upon treatment of 2,6-dichloropyridine with CH_3S^- under phase transfer condition afforded solely (I) in quantitative yield which then reacted with oligoethylene glycols to give the (II). Upon oxidation of (II) afforded the corresponding sulfones (III). The sulfonyl group in the sulfones (III) was substituted with thiolates and alkoxides very smoothly to give the macrocycles (IV).

Scheme