

SYNTHESIS AND OPTICAL RESOLUTION OF α -FLUORO- α -NITRO- α -(ARYLTHIO)-ACETATES

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As a part of synthetic studies for the multifunctional carbon compounds, some tri- and tetrafunctional α -nitroacetates(2 and 3) have been prepared. The first optical resolution of the tetrafunctionalized carbon structure has also succeeded.

Reaction of nitroacetates(1) with arylsulfenyl chlorides gave α -nitro- α -(arylthio)acetates(2) in excellent yields. The acetates(2) were easily converted into their potassium salts, which were fluorinated with perchloryl fluoride to produce α -fluoro- α -nitro- α -(arylthio)acetates(3) in moderate yields. The fluoroacetates(3) were also prepared by reaction of potassium salts of the α -fluoro- α -nitroacetates(4) with arylsulfenyl chlorides in good yields. The novel trifunctional(2) and tetrafunctional(3) carbon compounds obtained here are not yet known despite of their structural simplicity. The fluorinated derivatives(3) seem to be potent candidates for serving as building blocks for synthesizing fluorine-containing organic compounds.

Ethyl α -fluoro- α -nitro- α -(arylthio)acetate(3a : R=Et, R'=Ph) was then converted into the phenylethyl ester(5) by treatment with (+)- α -phenylethyl alcohol and $\text{Ti}(\text{OPr}^i)_4$ in high yield. The diastereomeric isomers(5a and 5b) were separated, and each isomer could be transformed to the optically active ethyl ester by treatment with EtOH and $\text{Ti}(\text{OEt})_4$ in excellent yield.

