NOVEL RING TRANSFORMATION OF α-MONO-SUBSTITUTED 1,2-BENZISOXAZOLE-3-ACETIC ACID ESTERS INTO 2H-AZIRINE DERIVATIVES

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Novel ring transformations of α-mono-substituted 1,2-benzisoxazole-3-acetic acid esters(1) are reported. It is found that on treatment with strong bases,such as NaH, t-BuOK, and EtONa, the esters (1) undergo three modes of reaction depending on the kind of the α-substituent as shown in Chart.

A) In the case of the esters (1) having α-alkyl, alkoky, phenoxy or phenylthio group, a Neber type rearrangement takes place to give 2H-azirine derivatives (2).

B) The esters (1) having α-dialkylamino group undergo a novel ring transformation to give 3-imino(2H)benzofuran derivatives (3).

C) Under similar conditions as above, the esters (1) having α-cyano or phenylsulfinyl group and a non-substituted ester (1, R=H) afford stable conjugated α-carbanions and are recovered unchanged.

These ring transformations giving 2H-azirine and benzofuran derivatives were the first example of a reaction concerning the nitrogen atom of 1,2-benzisoxazole ring. Several reactions of 2 and 3 are also reported.