LETTERS TO THE EDITOR

THERMOCATALYTIC AND THERMAL ISOMERIZATION OF 3-PHENYL-5-METHOXYISOXAZOLE

NEW METHOD FOR THE SYNTHESIS OF AZIRINE DERIVATIVES

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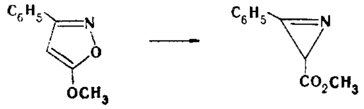
It is known that 3-aryl-5-alkoxyisoxazoles are isomerized at 200°C to 3-aryl-2H-arizine-2-carboxylic acid esters [1]. For the first time we have accomplished the thermocatalytic isomerization of 3-phenyl-5-methoxyisoxazole (I) to methyl 3-phenyl-2H-azirine-2-carboxylate (II) at 60° in the presence of cuprous stearate.



I II

A mixture of a solution of 0.5 g of isoxazole I [2] in 50 ml of cyclohexane and 0.05 g of cuprous stearate was heated in an argon atmosphere for 30 min, after which the solvent was removed, and the residue was chromatographed with a column filled with silica gel to give 0.3 g (60%) of azirine II, the physicochemical constants and spectral characteristics of which were in agreement with the literature data [1, 3]. The thermocatalytic isomerization of isoxazole I is a new method for the synthesis of azirine derivatives.

In addition to the catalytic isomerization, we also made a kinetic study of the thermal isomerization of isoxazole I to azirine II in order to establish the mechanism of the isomeric transformations. The kinetic experiments were carried out in sealed ampuls with a 0.05 M solution of isoxazole I in C_2Cl_4 at 443-458°K. The course of the isomerization was monitored by IR spectroscopy from the band at 1587 cm^{-1}, which is characteristic for isoxazole I. The isomerization rate constants were determined – $k_{443}° = (1.5 \pm 0.1) \cdot 10^{-5}\ sec^{-1}$, $k_{453}° = (2.9 \pm 0.2) \cdot 10^{-5}\ sec^{-1}$, and $k_{458}° = (4.9 \pm 0.5) \cdot 10^{-5}\ sec^{-1}$ – and the activation parameters were calculated – $E_a = 31 \pm 2$ kcal/mole, $\Delta H^{\neq} = 30 \pm 2$ kcal/mole, and $\Delta S^{\neq} = -14 \pm 4$ eu ($r = 0.97$). Considering the available literature data [4], our results make it possible to propose a diradical mechanism for the isomerization [1].

LITERATURE CITED

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