FORMATION OF SIX-MEMBERED RINGS BY THERMAL ISOMERIZATION OF 2H-AZIRINES: FORMATION OF ENAMINES AND THEIR REACTIONS

Kazuaki Isomura, Tatsuyoshi Tanaka, Shin-ichi Noguchi, Masumi Saruwatari, and Hiroshi Taniguchi

Department of Applied Chemistry, Faculty of Engineering, Kyushu University, Hakozaki, Higashiku, Fukuoka, Japan.

Thermal isomerization reactions of 2-(3,4,6-trimethylbenzofuran-2-yl)- 1a, 2-(3-ethyl-4.6-dimethylbenzofuran-2-yl)- 1b, 2-(4,6-dimethyl-3-*i*-propylbenzofuran-2-yl)- 1c, 2-(3-ethylbenzofuran-2-yl)- 1d, and 2-(3-*t*-butyl-6-methylbenzofuran-2-yl)-3-carbethoxy-2H-azirine 1e were performed. When a $CDCl_3$ solution of 1a was let stand at 35.5°C, quantitative formation of 3-carbethoxy-7,9-dimethylbenzofuro[3,2-c]pyridine 2a was observed. Under the same conditions, 1b and 1c gave ethy α-amino-β-(4,6-dimethyl-3-vinylbenzofuran-2-yl)acrylate 3b and ethyl α-amino-β-(4,6-dimethyl-*i*-propenylbenzofuran-2-yl)acrylate 3c, respectively, in quantitative yields. When the enamines 3b and 3c were heated at higher temperatures, cyclization into six-membered rings were observed giving 3-carbethoxy-1,7,9-trimethylbenzofuro[3,2-c]pyridine 2b and 3-carbethoxy-1,1,7,9-tetramethyl-1,2-dihydrobenzofuro[3,2-c]pyridine 4c, respectively. In the case of 1d, reaction at 35.5°C gave a 4 : 1 mixture of ethyl α-amino-β-(3-vinylbenzofuran-2-yl)-acrylate 3d and 3-carbethoxy-1-methylbenzofuro[3,2-c]pyridine 2d. The ratio of 3d to 2d did not change on prolonged standing at 35.5°C. Thermal reaction of 1e gave ethyl (3-*t*-butyl-6-methylbenzofurna-2-yl)cyanoacetate 5e.

From these results, the formation of six-membered rings from 2H-azirines via vinyl nitrene intermediates was considered to proceed by step-wise hydrogen shift.

The reaction of the enamine 3c with $PdCl_2(PhCN)_2$ to form dibenzofuran and benzofuroazepine derivatives was also investigated.