Thermal Decarboxylation of an Aziridine Ester

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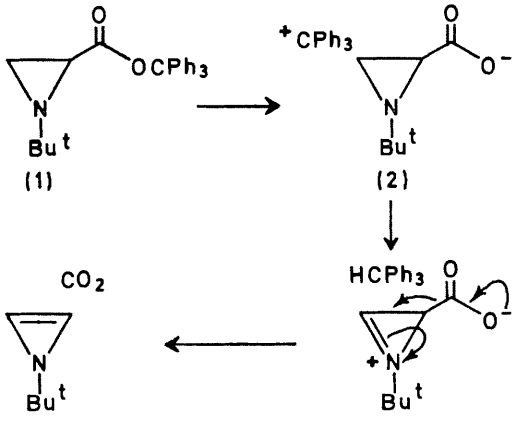
Summary An attempt to prepare a 2-azirine *via* thermolysis of an aziridinecarboxylate ester has revealed two previously unknown decomposition paths open to aziridine esters.

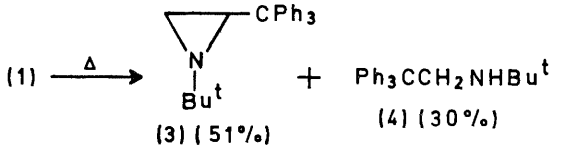
IN spite of considerable theoretical interest, little is known concerning the potentially antiaromatic 2-azirine ring.[1] As one possible approach to the generation of this molecule, the sequence depicted in Scheme 1 was devised. This



SCHEME 1

scheme was based on previously reported ionic thermal ionization of esters,[2] the hydride-accepting properties of the trityl cation,[3] and the known stability of the aziridinyl cation.[4]

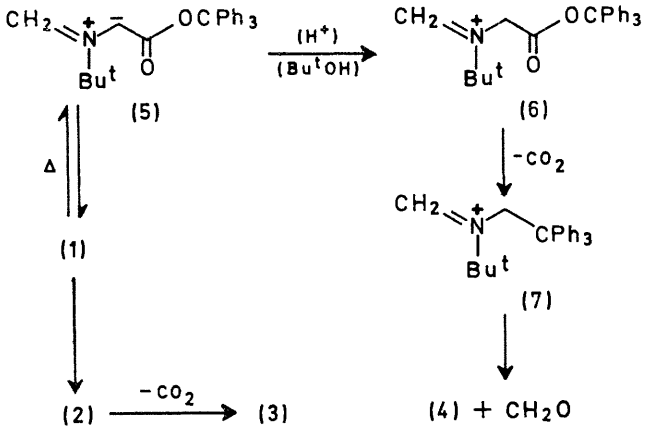
Preparation of ester (1) (m.p. 117—118°) was accomplished by the reaction of sodium 1-t-butylaziridine-2-carboxylate[5] with trityl bromide in 52% yield. A benzene solution of this ester was heated in a sealed tube at 180° for 14 h. Two products, (3) and (4), were isolated from this reaction mixture.†



Although these products do not implicate a 2-azirine intermediate, they were sufficiently interesting to warrant further investigation. It was first demonstrated that (3) was stable under the reaction conditions. Repetition of the pyrolysis in cumene resulted in the same product distribution and no detectable (less than 1% theoretical) bicumyl. While this experiment does not exclude a radical cage process, the absence of bicumyl and the results of previous ester decarboxylation studies[2] argue against a homolytic process.

Since an ionic path would necessarily require a strongly basic carbanionic intermediate, we attempted to intercept this intermediate *via* protonation. Pyrolysis of (1) in the presence of an equivalent amount of Bu^tOH yielded (almost quantitatively) (3) and (4) in a 1:8 ratio. In addition, the aqueous layer yielded formaldehyde (isolated as the dimedone derivative).

On the basis of these results, the paths outlined in Scheme 2 seem to best accommodate the available evidence. The protonation of reversibly formed azomethine ylides [*e.g.*, (5)] by alcohols or adventitious moisture has ample precedent.[6] The decarboxylation of (2) and (6) are presumably aided by the inductive effects of the aziridine ring and the quaternary nitrogen, respectively. Irrespective of the details of the decarboxylation steps, it is clear that both proceed *via* efficient (apparently ion-pair) mechanisms. If the above interpretation of our results is correct, it seems possible that certain aziridinecarboxylate derivatives may be precursors of synthetically useful aziridine carbanions.



SCHEME 2

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† Satisfactory analytical and spectral data were obtained in support of the compounds reported herein.

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