Thermal Rearrangements of Arylaroylaziridines into 2,5-Diaryloxazoles

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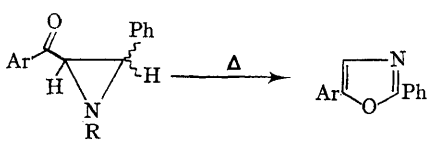
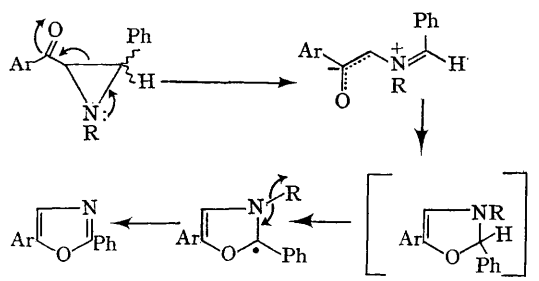
MANY examples of thermal rearrangements of small ring compounds to yield systems with less bond-angle strain have been reported.[1] In the vinylaziridine system, these reactions involve ring expansion to form 1-azacyclopentene and Δ^3-pyrroline derivatives.[2] These rearrangements are structurally analogous to vinylcyclopropane–cyclopentene isomerization[3] and involve scission of the carbon–nitrogen bond in the aziridine ring. We report on a related transformation in the aziridine ring system involving carbon–carbon bond cleavage.



Ar=Ph,C_6H_4Me R=Bu^t,CH_2Ph,C_6H_{11},Me



Thermolysis of *trans*-1-t-butyl-3-benzoyl-2-phenylaziridine at 220° is readily effected in a heated injector unit of a gas chromatograph. The major product (96%) was collected and identified as 2,5-diphenyloxazole by comparison of the i.r. spectrum and retention time with that of an authentic sample. The loss of the nitrogen substituent and the formation of the corresponding oxazole in the thermolysis of a number of substituted *cis*- and *trans*-aroylarylaziridines† has been found to be a general phenomenon.

The formation of the oxazole and the complete absence of the isoxazole ring suggests that the

† These were prepared according to the general procedure of P. L. Southwick and D. R. Christman, *J. Amer. Chem. Soc.*, 1952, **74**, 1886.

reaction proceeds by exclusive C–C bond scission. Subsequent ring closure to a 2,3-dihydro-oxazole followed by thermal elimination readily accounts for the observed product. The ready oxidation of the 2,3-dihydro-oxazole may be attributed both to the extremely low bond-dissociation energy of the tertiary C–H bond and the stability of the heteroaromatic system formed. The formation of a stabilized 1,3-dipole intermediate[4] provides a reasonable explanation for the direction of ring opening.

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