A Novel Pyrolytic Rearrangement of *trans*-1,3-Dibenzoyl-2-phenylaziridine

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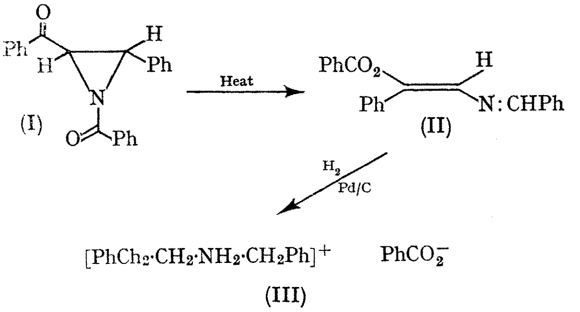
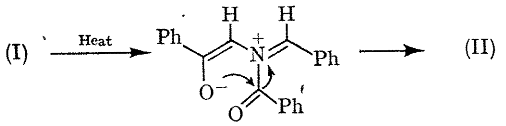
Summary *trans*-1,3-Dibenzoyl-2-phenylaziridine undergoes thermal rearrangement to 1,4-diphenyl-4-benzoyloxy-2-azabutadiene *via* carbon–carbon bond cleavage of the aziridine ring.

RECENT work has demonstrated that appropriately substituted aziridines form adducts with various alkenes and alkynes when heated in inert solvents.[1] These reactions can be envisaged as occurring by an initial cleavage of the carbon–carbon bond of the aziridine ring to form a 1,3-dipolar intermediate which subsequently adds to the unsaturated substrate. In the course of experiments designed to investigate the behaviour of these intermediates, we attempted to trap the 1,3-dipolar species that would be expected to be formed from the thermolysis of *trans*-1,3-dibenzoyl-2-phenylaziridine (I).

When (I) was treated with dimethyl acetylenedicarboxylate in refluxing toluene, a crystalline product (II), m.p. 110--111°, was formed in high yield, and was subsequently shown to be isomeric with starting material. Undoubtedly this product resulted from intramolecular rearrangement of (I), since this same compound was obtained when the reaction was repeated in the absence of dimethyl acetylene dicarboxylate. The structure of this material is assigned as 1,4-diphenyl-4-benzoyloxy-2-azabutadiene (II) on the basis of its microanalysis and the following spectral data: mass spectrum *m/e* 327; i.r. λ_{max} (KBr) 5·80, 6·10, 8·48, 12·96, and 13·27 μm; u.v.: λ_{max} (ethanol) 338 (ϵ 28,700) and 230 nm (ϵ 24,600); n.m.r. ($CDCl_3$) multiplets centred at τ 1·72 (3H) and 2·60 (14 H). Chemical confirmation was obtained by catalytic hydrogenation of (II). The product isolated was identified as the benzylphenethylammonium salt of benzoic acid (III) on the basis of its spectral data and by an independent synthesis of (III) from benzylphenethylamine and benzoic acid.





The mechanism suggested for the rearrangement involves cleavage of the carbon–carbon bond of the aziridine ring to give a 1,3-dipolar intermediate, which rearranges to the final product by the way of a benzoyl migration. The inability of an external trapping reagent such as dimethyl acetylenedicarboxylate to trap the 1,3-dipolar intermediate suggests that either the isomerization is a concerted process or else the 1,3-dipole rearranges faster than it can be trapped.

The thermal rearrangement of dibenzoylaziridine (I) stands in marked contrast to previous work on related 1,3-diaroyl-2-arylaziridines.[2] In those cases the rearrangement was postulated to give α-benzamidobenzalacetophenones. It was suggested that the reaction proceeds by transfer of the aziridinyl hyrdogen to the amido-oxygen with concurrent breaking of the carbon–nitrogen bond of the three-membered ring.[2]

We thank the Petroleum Research Fund, administered by the American Chemical Society, and the Alfred P. Sloan Foundation for financial support.

(*Received, August 22nd,* 1969; *Com.* 1287.)

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