

REACTIONS OF ARYLAROYLAZIRIDINES WITH
DIPHENYLIODONIUM IODIDE

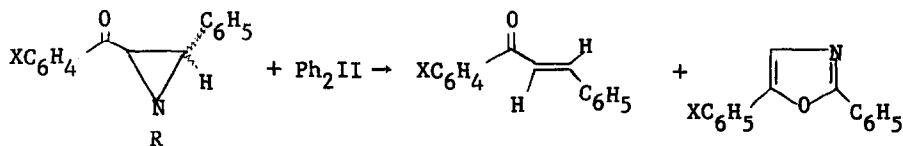
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1-Aroylaziridines are known to be readily isomerized into 2-aryl- Δ^2 -oxazolines by the action of aluminum halides¹ or by nucleophilic reagents such as iodide ion.^{2,3} Suitably substituted 1-acyl-2-alkylaziridines undergo pyrolytic isomerization to unsaturated amides.⁴ The successful application of these reactions to 2-aryloxazolines has not been reported in the literature. We now wish to report on a novel diphenyliodonium iodide catalyzed rearrangement of suitably substituted 2-benzoylaziridines to form 2,5-diaryloxazoles and the corresponding α,β -unsaturated ketone.

Treatment of trans-1-benzyl-2-phenyl-3-benzoylaziridine with diphenyliodonium iodide in refluxing tetrahydrofuran resulted in the formation of trans-benzalacetophenone (73%), 2,5-diphenyl oxazole (7%), and iodobenzene(83%).



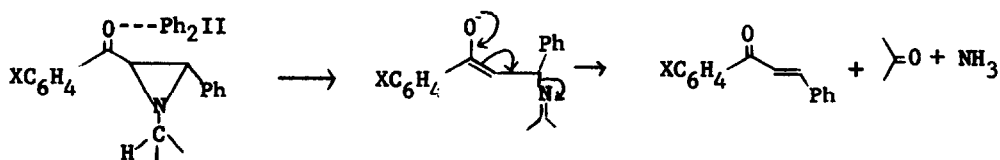
The removal of the nitrogen atom and the subsequent formation of the corresponding olefin in the reaction between an arylaroylaziridine and diphenyliodonium iodide is found to be a general phenomenon. The accompanying table summarizes data on the products obtained with a number of substituted cis-trans-arylaroylaziridines.⁵

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Table I

	<u>Arylaroylaziridine</u>	<u>% yield of oxazole</u>	<u>% yield of substituted trans-benzal acetophenone</u>
I _A	X=H, R=CH ₂ C ₆ H ₅ (trans)	7	73
I _B	X=H, R=CH ₂ C ₆ H ₅ (cis)	8	75
II _A	X=H, R=C ₆ H ₁₁ (trans)	-	76
II _B	X=H, R=C ₆ H ₁₁ (cis)	-	72
III _A	X=CH ₃ , R=CH ₂ C ₆ H ₅ (trans)	44	52
III _B	X=CH ₃ , R=CH ₂ C ₆ H ₅ (cis)	41	54
IV _A	X=CH ₃ , R=C ₆ H ₁₁ (trans)	-	67
IV _B	X=CH ₃ , R=C ₆ H ₁₁ (cis)	-	65

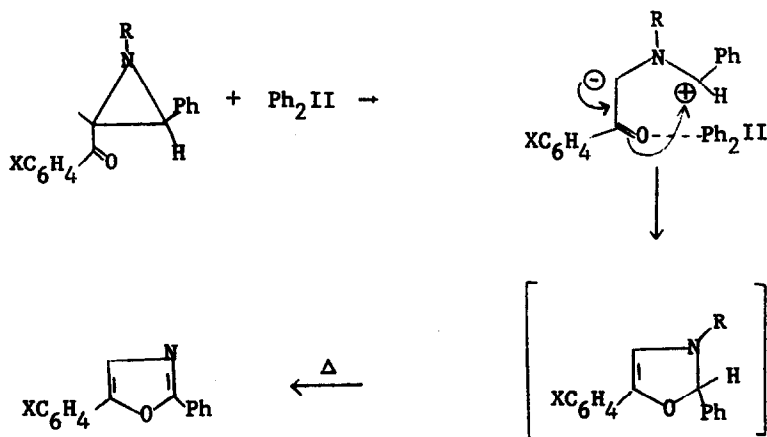
The isolation of an α - β unsaturated ketone from the reaction mixture suggests that the reaction proceeds by coordination of diphenyliodonium iodide with the unshared electrons of the carbonyl oxygen followed by proton loss and subsequent elimination, as formulated below.



Support for the above contention was found in the observation that 1-cyclohexyl-2-phenyl-3-benzoylaziridine (II) gave trans-benzalacetophenone and cyclohexanone in comparable yields. Similarly, 1-benzyl-2-p-toluy1-3-phenyl aziridine (III) afforded benzaldehyde and ammonia. Further confirming evidence for the above mechanism was obtained by the finding that an authentic sample of N-1-(2-benzoyl-1-phenylethyl)cyclohexanimine⁶ was converted rapidly and quantitatively to trans-benzalacetophenone and cyclohexanone when subjected

to the reaction conditions.

It is premature to propose a precise mechanism to encompass the diphenyliodonium iodide catalyzed transformation of arylaroylaziridines to diaryloxazoles. As a working hypothesis, however, one could envision diphenyliodonium iodide coordinating with the carbonyl group thereby promoting carbon-carbon cleavage of the strained aziridine ring. Subsequent ring closure to a 2,3-dihydrooxazole followed by oxidation readily accounts for the observed product. The possibility that the 2,3-dihydrooxazole was formed by



an iodide ion catalyzed isomerization was discounted by the observation that the reaction of arylaroylaziridines with sodium iodide in acetone did not afford the same products.

It is noteworthy that in the reaction of aziridines I and III, toluene is formed as a byproduct. The fact that N-cyclohexyl aziridines II and IV afford only α,β -unsaturated ketones suggests that the initial 2,3-dihydrooxazole may either undergo further oxidation or revert back to starting material.⁷ A similar reversal has been reported in the related oxazoline system.⁸ Interestingly, the yield of diaryloxazole is much higher with aziridine I than with III. A reasonable interpretation of this is that a considerable amount

of positive character appears on the carbonyl oxygen in the transition state for rearrangement. This is compatible with the above mechanism if it is assumed that diphenyliodonium iodide behaves as a weak Lewis acid and by coordinating with the carbonyl oxygen promotes ring cleavage. Alternatively, it may be argued that an ion pair mechanism may be in operation, with carbon-oxygen bond formation preceding carbon-carbon bond breakage.

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References:

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5. Satisfactory analyses were obtained for all new compounds, NMR, IR, UV spectral comparisons and mixture melting points with authentic samples confirmed the identity of the products obtained.
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7. In this case, the N-cyclohexyl substituted aziridine would be expected to be resistant toward further oxidation.
8. H.L. Wehrmeister, J. Org. Chem., 30, 664 (1965).