1043, 992, and 310 cm^{-1}. The chloroplatinate crystallized from water, mp 184–185° dec.

Anal. Calcd for $C_{20}H_{26}Cl_6N_2O_2Pt$: C, 32.8; H, 3.6; Pt, 26.6. Found: C, 32.2; H, 4.0; Pt, 26.7.

Preparation of 6-(5-Carbethoxypent-4-enyl)-2-picoline (19).—The aldehyde **17** and phosphorane, in equimolar amounts, were heated in refluxing ethanol for 6 hr. After removal of the solvent, and drying of the residue by azeotropic distillation with benzene, petroleum ether (40–60°) was added to the viscous residue causing triphenylphosphine oxide to precipitate. After removal of the precipitate and the solvent, a honey-colored oil (84%) remained. Chromatography over B. D. H. silica gel with chloroform gave a pale yellow oil (62%) which was sufficiently pure for most purposes. An analytical sample was obtained by molecular distillation (10^{-4} mm): $n^{20}\text{D}$ 1.5211; $\lambda_{\max}^{\text{EtOH}}$ 210, 266, and 272 mμ (log ε 4.1, 3.5, and 3.4).

Anal. Calcd for $C_{14}H_{19}NO_2$: C, 72.1; H, 8.2; N, 6.0. Found: C, 72.2; H, 8.0; N, 6.2.

Bromination of the α,β-Unsaturated Ester 19.—The ester **19** (0.34 g) was dissolved in water (5 ml) by adding dioxane (*ca.* 10 ml). To the vigorously stirred solution was added bromine (0.25 g) in dioxane (5 ml) over a period of 5 min. After stirring for 0.5 hr, the solvent and excess bromine were removed under vacuum. The impure crystals were triturated with chloroform and filtered to yield a buff-colored product (0.46 g, 88%), mp 128–130°. Recrystallization from acetonitrile and from acetone gave an analytical sample of 6-methyl-4-carbethoxybromomethyl-1,2,3,4-tetrahydroquinolizinium bromide (**20**) as white crystals: mp 132–132.5°; $\lambda_{\max}^{H_2O}$ 275 mμ (log ε 3.8); $\nu_{\max}$ 2960, 2906, 2840, 1615, 1582, 1489, 1302, 1257, 1212, 1030, and 802 cm^{-1}.

Anal. Calcd for $C_{14}H_{19}Br_2NO_2$: C, 42.7; H, 4.9; N, 3.6; Br, 40.6. Found: C, 42.9; H, 5.1; N, 3.8; Br, 40.8.

The perchlorate precipitated from aqueous solution and could be crystallized from water. It decomposed explosively at *ca.* 180° without melting: $\lambda_{\max}^{H_2O}$ 275 mμ (log ε 3.8); $\nu_{\max}$ 2962, 2907, 2842, 1616, 1583, 1490, 1306, 1090, 1030, and 800 cm^{-1}.

Anal. Calcd for $C_{14}H_{19}BrClNO_6$: N, 3.4. Found: N, 3.4.

The chloroform extracts were chromatographed over B. D. H silica gel and purified by molecular distillation (10^{-4} mm) to give a pale pink oil. A mass spectral determination gave the following data: *m/e* (% of base peak) 395 (1), 393 (2), 391 (1), 315 (5), 311 (5), 268 (3), 233 (16), 120 (10), and 107 (100).

Treatment of 20 with Base.—Several combinations of base and solvent were studied, but the results were always the same.

The salt **20** (100 mg) was dissolved in water (1.5 ml) and to this was added dropwise a solution of potassium carbonate (50 mg) in water (2 ml). At the end of the addition an oil separated. The product was extracted with carbon tetrachloride, the solvent was removed, and the product was dried by azeotropic distillation with benzene. The product was obtaned as a pale yellow oil (50 mg, 63%) after chromatography over B. D. H. silica gel with carbon tetrachloride: nmr, olefinic and aromatic protons (τ 2.5–3.5) (4 H), a quartet (τ 5.86, *J* = 7 Hz) (2 H), a triplet (τ 7.3, *J* = 7 Hz) (2 H), a singlet (τ 7.5) (3 H), a complex multiplet (τ 7.5–8.4) (4 H), and a triplet (τ 8.7, *J* = 7 Hz); mass spectrum, *m/e* (% of base peak), 107 (100), 108 (32), 120 (18), 158 (10), 230 (32), 231 (9), 311 (12), and 313 (12).

Anal. Calcd for $C_{14}H_{18}BrNO_2$: C, 53.9; H, 5.8; Br, 25.6; N, 4.5. Found: C, 53.7; H, 5.6; Br, 25.2; N, 4.5.

Registry No.—**3**, 15981-94-9; **4**, 15981-95-0; **5** perchlorate, 15982-08-8; **5** chloroplatinate, 12244-22-3; **6** bromide, 15981-96-1; **10**, 15981-97-2; **11**, 15981-98-3; **12**, 15982-00-0; **13**, 15982-01-1; **14**, 15982-02-2; **15**, 15981-99-4; **16**, 15982-03-3; **17** chloroplatinate, 12244-21-2; **19**, 15982-04-4; **20** bromide, 15982-05-5; **20** perchlorate, 15982-06-6; **21**, 15982-07-7.

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Reaction of Aziridine and Oxirane Derivatives with Diphenyliodonium Iodide[1,2]

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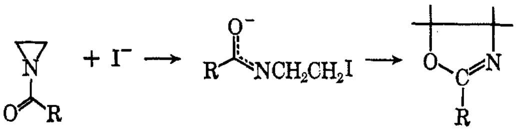
The reaction of diphenyliodonium iodide with suitably substituted 2-benzoylaziridines affords 2,5-diaryloxazoles and the corresponding α,β-unsaturated ketone. The removal of the nitrogen atom and the subsequent formation of the corresponding olefin is found to be a general phenomenon. The mechanism proposed for the deamination involves coordination of diphenyliodonium iodide with the unshared electrons of the carbonyl oxygen followed by proton loss and subsequent elimination. The formation of the substituted 2,5-diaryloxazole proceeds by carbon–carbon cleavage of the aziridine ring to produce an intermediate tight ion pair. The reaction between diphenyliodonium iodide and α,β-epoxy ketones causes a major fragmentation of the oxide ring and affords a mixture of aryl acids and ketones.

1-Aroylaziridines are known to be readily isomerized into 2-aryl-Δ^2-oxazolines by the action of aluminum halides, heat, or nucleophilic reagents.[4–11] These rearrangements are formally analogous to the vinylcyclopropane–cyclopentene isomerization and the details of the transformation have been elegantly elucidated by Heine and coworkers.[11] The isomerization by nucleophilic reagents has been explained by a reaction scheme involving attack by a nucleophile, such as iodide ion, on one of the carbon atoms of the aziridine ring to form a 2-iodoethylamine anion (eq 1). In a subsequent step the ion cyclizes to the oxazoline and regenerates the iodide ion. Substituted 1-acyl-2-alkylaziridines also undergo pyrolytic isomerization to form N-allylamides.[12,13] Kinetic and stereochemical



(1)

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[1] Support of this research by a grant from the National Institute of Health (Grant GM-13990-01) is acknowledged with appreciation.

[2] For a preliminary report of this work, see A. Padwa and L. Hamilton, *Tetrahedron Lett.*, 1861 (1967).

[3] National Institute of Health Predoctoral Fellow, 1964–1967.

[4] H. Heine and Z. Proctor, *J. Org. Chem.*, **23**, 1554 (1958).

[5] H. Heine, M. E. Fetter, and E. Nicholson, *J. Amer. Chem. Soc.*, **81**, 2202 (1959).

[6] H. Heine, W. G. Kenyon, and E. M. Johnson, *ibid.*, **83**, 2570 (1961).

[7] P. Thrum and A. R. Day, *J. Med. Chem.*, **8**, 107 (1965).

[8] R. D. Guthrie and D. Murphy, *J. Chem. Soc.*, 3828 (1965).

[9] P. E. Fanta and E. N. Walsh, *J. Org. Chem.*, **30**, 3574 (1965).

[10] P. E. Fanta and E. N. Walsh, *ibid.*, **31**, 59 (1966).

[11] H. Heine, *Angew. Chem. Intern. Ed. Engl.*, **1**, 528 (1962).

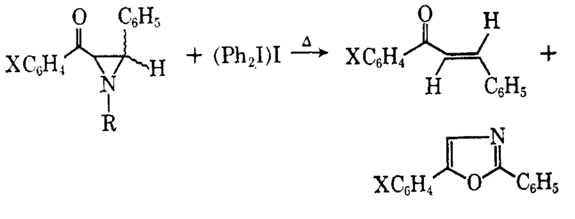
[12] P. E. Fanta, "Heterocyclic Compounds with Three and Four Membered Rings," part I, A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, pp 524–575.

[13] P. E. Fanta and M. K. Kathan, *J. Heterocycl. Chem.*, **1**, 293 (1964).

investigations suggest that the rearrangement is an intramolecular, concerted *cis* elimination involving transfer of a proton from the alkyl group to the amido oxygen.[13] The successful application of these reactions to the related 2-aroylaziridine system has not been reported in the literature.[2] In view of the close structural relationship between these two sets of compounds, it became of interest to determine whether similar processes would occur with 2-aroylaziridines. The present paper describes a novel diphenyliodonium iodide catalyzed rearrangement of suitably substituted 2-benzoylaziridines to form 2,5-diaryloxazoles and the corresponding α,β-unsaturated ketone. Extension of this reaction into the related oxirane system resulted in a major fragmentation of the oxide ring.

When the reaction of *trans*-1-benzyl-2-phenyl-3-benzoylaziridine (I) and sodium iodide was carried out using anhydrous acetone, there was obtained a complex mixture of products. Thin layer chromatography of the crude reaction mixture suggested the presence of between eight and ten products. Numerous attempts to induce a ring expansion of a variety of other *cis*- and *trans*-arylaroylaziridines with sodium iodide afforded only brown, tarry materials which defied all attempts at characterization. Thus *cis*-1-cyclohexyl-2-phenyl-3-*p*-toluylaziridine (VIII) with sodium or potassium iodide in ether, acetone, or dioxane produced only recovered starting material and brown tars. Similar results were obtained in acetone or tetrahydrofuran solutions containing potassium thiocyanate as the nucleophilic reagent. Since 1-aroylaziridines are isomerized by Lewis acids, it was felt that a mild electrophilic species, such as diphenyliodonium iodide, may effect the desired transformation.

Treatment of *trans*-1-benzyl-2-phenyl-3-benzoylaziridine (I) with an equivalent amount of diphenyliodonium iodide in refluxing tetrahydrofuran resulted in the complete disappearance of starting material. The products were separated by liquid-liquid partition chromatography and purified by crystallization. The products of the reaction were *trans*-benzalacetophenone (73%), 2,5-diphenyloxazole (7%), and iodobenzene (83%). Structures of the products (eq 2) follow from their spectral properties and by comparison with authentic samples. Under the same reaction conditions described above, but without diphenyliodonium iodide, only recovered aziridine I was obtained. On the other hand, refluxing a toluene solution of I in the presence or absence of diphenyliodonium iodide afforded only brown tarry material. When diphenyliodonium iodide was heated to reflux in toluene, a high yield of iodobenzene (70%) was obtained after 6 hr.[14] This observation indicates that in a high boiling solvent, such as toluene, the decomposition of diphenyliodonium iodide to iodobenzene proceeds at a rate faster than reaction with the arylaroylaziridine. It must be concluded that diphenyliodonium iodide is involved in the reaction with arylaroylaziridines prior to its decomposition. This was demonstrated by heating a solution of I and iodobenzene in tetrahydrofuran and recovering starting aziridine in better than 98% yield. Thereafter, tetrahydrofuran was used as solvent so as to retard the decomposition of diphenyliodonium iodide and to promote its reaction with the arylaroylaziridine.



(2)

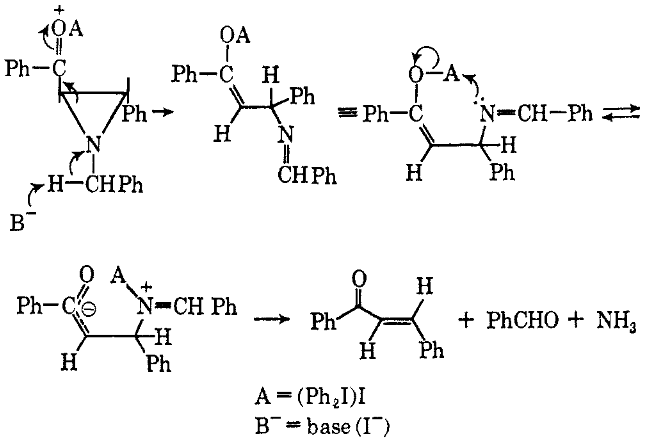
The removal of the nitrogen atom and the subsequent formation of the corresponding olefin in the reaction between an arylaroylaziridine and diphenyliodonium iodide is found to be a general phenomenon. Table I summarizes data on the products obtained with a number of substituted *cis,trans*-arylaroylaziridines. The isolation of an α,β-unsaturated ketone from the reaction mixture suggest 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 in Scheme I. Support for the above contention was found in the observation that 1-cyclohexyl-2-phenyl-3-benzoylaziridine (III) gave *trans*-benzalacetophenone and cyclohexanone in comparable yields. Similarly, *trans*-1-benzyl-2-*p*-toluyl-3-phenylaziridine (V) 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)cyclohexanimine[15] was converted rapidly and quantita-

Table I

Reactions of Arylaroylaziridines with Diphenyliodonium Iodide

Compd	Substituents	Yield of oxazole, %	Yield of substituted *trans*-benzalacetophenone, %
I	X = H; R = $CH_2C_6H_5$ (*trans*)	7	73
II	X = H; R = $CH_2C_6H_5$ (*cis*)	8	75
III	X = H; R = C_6H_{11} (*trans*)		76
IV	X = H; R = C_6H_{11} (*cis*)		72
V	X = CH_3; R = $CH_2C_6H_5$ (*trans*)	44	52
VI	X = CH_3; R = $CH_2C_6H_5$ (*cis*)	41	54
VII	X = CH_3; R = C_6H_{11} (*trans*)		67
VIII	X = CH_3; R = C_6H_{11} (*cis*)		65

Scheme I



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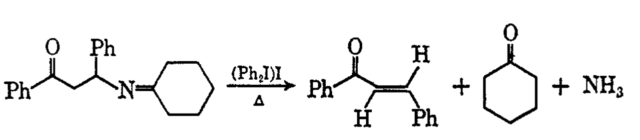
[14] F. M. Beringer, A. Brierley, M. Drexler, E. M. Gindler, and C. C. Lumpkin, *J. Amer. Chem. Soc.*, **75**, 2708 (1953).

[15] A. Padwa and L. Hamilton, *ibid.*, **89**, 102 (1967).

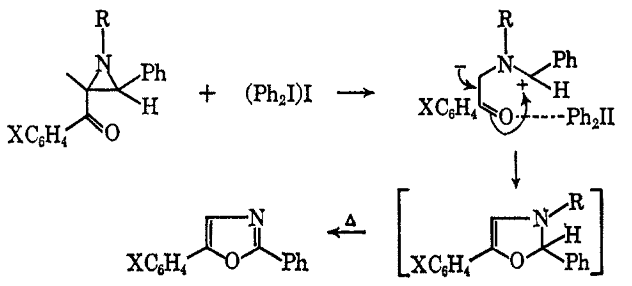
tively into *trans*-benzalacetophenone and cyclohexanone when subjected to the reaction conditions[16] (eq 3).



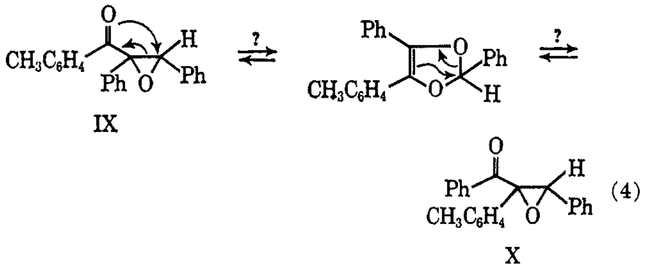
(3)

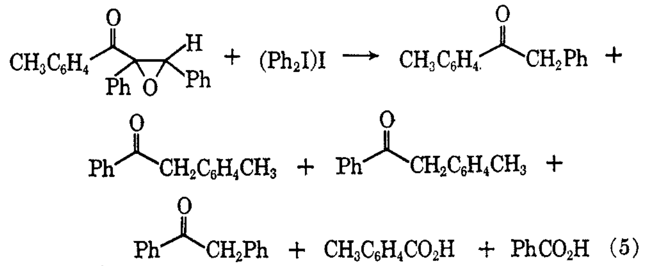
One possible sequence of steps to explain the diphenyliodonium iodide catalyzed transformation of arylaroylaziridines to diaryloxazoles involves coordination of diphenyliodonium iodide with the carbonyl group (Scheme II). Such coordination can induce cleavage of the carbon–carbon bond of the strained 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, as suggested by Heine for the rearrangement of N-aroylaziridines to Δ^2-oxazolines, was discounted by the observation that the yield of diaryloxazole did not increase when sodium iodide was added to the reaction mixture. Interestingly, the yield of diaryloxazole is much higher with aziridines V and VI than with aziridines I and II. A reasonable explanation 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. This, in turn, is strongly supported by the fact that other Lewis acids, such as $ZnCl_2$ or $AlBr_3$, can also promote the rearrangement to 2,5-diaryloxazoles. Alternatively, it may be argued that an ion-pair mechanism may be in operation, with carbon–oxygen bond formation preceding carbon–carbon bond breakage.

SCHEME II



It is noteworthy that in the reaction of aziridines I and V, toluene is formed as a by-product. The fact that N-cyclohexylaziridines III and VII afford only α,β-unsaturated ketones suggests that the initial 2,3-dihydrooxazole may either undergo further oxidation or revert back to starting material. In the N-cyclohexyl system, the 2,3-dihydrooxazole would be expected to be resistant toward further oxidation. A similar reversal has been reported in the related oxazoline system.[17] These observations plus the knowledge that cyclopropyl carboxyaldehyde has been found to be in equilibrium with dihydrofuran at high temperatures[18] suggested that a reaction sequence could be designed which would involve a diphenyliodonium iodide catalyzed expansion of an α,β-epoxy ketone to a substituted 1,3-dioxolene. Once formed, the five-membered ring could revert back to an α,β-epoxy ketone in either of two directions. In order to test for this possibility, we investigated the possible conversion of IX into X (eq 4). The technique chosen to follow the proposed rearrangement involved nmr analysis of the reaction mixture. Treatment of IX with diphenyliodonium iodide at 240° for 30 min resulted in the complete disappearance of the resonance associated with the epoxide proton (τ 5.50). The nmr spectrum of the crude reaction mixture had a new, one-proton singlet at τ 5.78 and a broad three-proton signal at 7.68. Careful scrutiny by vapor phase chromatography, however, failed to reveal the presence of X. Chromatography of the mixture on a silica gel column afforded 4-methyldesoxybenzoin (18%), 4′-methyldesoxybenzoin (2%), desoxybenzoin (30%), *p*-toluic acid (32%), and benzoic acid (18%) (see eq 5).





Furthermore, the only reaction observed between diphenyliodonium iodide and other suitably substituted α,β-epoxy ketones was fragmentation of the oxide ring and the formation of a mixture of aryl acids and ketones. The results are displayed in Table II and details are given in the Experimental Section. The foregoing data are taken to imply that ring expansion of α,β-epoxy ketones does not occur in the presence of either diphenyliodonium iodide or other Lewis acids.

The conversion of α,β-epoxy ketones into a mixture of aryl ketones and acids requires a major fragmentation of the oxide ring. This result may be rationalized by a number of different routes shown in Scheme III. One possibility (route A) involves the acid- (Lewis) catalyzed migration of an aroyl group to produce a β-diketone, which under work-up conditions affords the observed products.[19] The fact that 1,2-diphenyl-1,3-

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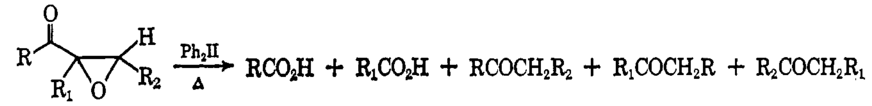
[16] The fact that the imine undergoes an elimination does not necessarily exclude an initial coordination of the Lewis acid with the nitrogen atom as a significant mechanistic process.

[17] H. L. Wehrmeister, *J. Org. Chem.*, **30**, 664 (1965).

[18] C. L. Wilson, *J. Amer. Chem. Soc.*, **69**, 3002 (1947).

[19] The preferential migration of an aroyl group is not without precedent. See, for example, J. D. Roberts, D. R. Smith, and C. C. Lee, *ibid.*, **73**, 618 (1951); H. O. House and D. J. Reif, *ibid.*, **77**, 6525 (1955).

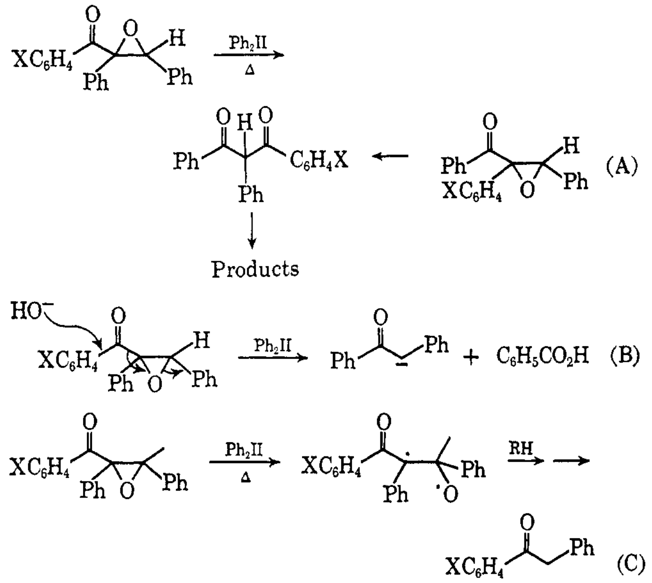
Table II
Reaction of Substituted Epoxy Ketones with Diphenyliodonium Iodide[a]



Substituents (starting epoxide)	% yield RCO$_2$H	R$_1$CO$_2$H	RCOCH$_2$R$_2$	R$_1$COCH$_2$R	R$_2$COCH$_2$R$_1$
R = C$_6$H$_4$CH$_3$; R$_1$ = R$_2$ = C$_6$H$_5$ (IX)	32	18	18	...	30
R = R$_2$ = C$_6$H$_5$; R$_1$ = C$_6$H$_4$CH$_3$ (X)	36	14	12	10	27
R = R$_1$ = C$_6$H$_5$; R$_2$ = C$_6$H$_4$CH$_3$ (XI)	49	...	46	4	...
R = CH$_3$; R$_1$ = R$_2$ = C$_6$H$_5$ (XII)[b]	24	24	15	...	33
R = R$_2$ = C$_6$H$_5$; R$_1$ = CH$_3$ (XIII)[c]	35	15	19	17	11

[a] All reactions were carried out in sealed tubes at 240° for 30 min. [b] Prepared by the procedure described by H. E. Zimmerman, L. Singer, and B. S. Thyagarajan [*J. Amer. Chem. Soc.*, **81,** 108 (1959)]. [c] Prepared by the procedure described by H. O. House and D. J. Reif [*ibid.*, **77,** 6525 (1955)].

Scheme III



butanedione (XIV) gives the same products as does XII and XIII when exposed to similar experimental conditions adds credence to this proposition. However, if this were the only available route, one would expect epoxy ketones IX and X (or XII and XIII) to give an identical product distribution. Experimentally (Table II), reaction of XII afforded a mixture of aryl ketones substantially different from that obtained from XIII. Thus it seems that the migration of an aroyl group in the diphenyliodonium iodide reaction of an α,β-epoxy ketone only provides for a partial explanation of the observed results. Another mechanistic possibility (route B) involves attack of a nucleophile on the carbon atom of the aroyl group with concomitant ring opening. The basic hydrolysis of 2-cyclohexyl-3-phenyl-3-benzoyloxazirane bears similar characteristics and provides ample precedent for this route.[20] Route C involves cleavage of the carbon-oxygen bond of the epoxide ring followed by hydrogen abstraction and β scission. These explanations can not be differentiated by product analysis and consequently it is not possible to choose among them. The relative importance of each route seems to depend on the particular system involved. In fact, it is quite probable that all three routes may be occurring to a varying degree at the same time.

Experimental Section[21]

Reaction of 1-Benzyl-2-*p*-toluyl-3-phenylaziridine (V) with Diphenyliodonium Iodide in Tetrahydrofuran.—A mixture of 0.50 g of *trans*-aziridine (V) and 0.62 g of diphenyliodonium iodide in 200 ml of tetrahydrofuran was heated to reflux for 72 hr. Thin layer chromatography demonstrated the complete disappearance of starting material and the appearance of three major new spots. Removal of the solvent *in vacuo* left a red oil which was subjected to liquid-liquid column chromatography. The chromatogram showed three well-resolved peaks with retention volumes of 1800 2400, and 2800 ml. The first fraction (0.37 g, 60%) was shown to be pure iodobenzene by comparison of its infrared spectrum with that of an authentic sample. The second peak in the chromatogram (0.15 g, 44%) was a colorless oil which solidified upon standing. Recrystallization from 95% ethanol gave white crystals, mp 81–82°. Comparison of the nmr, uv, and ir spectra of this species with an authentic sample of 2-phenyl-5-*p*-tolyloxazole established its identity. The mixture melting point of these two materials was undepressed at 81–82°. The last fraction in the chromatogram (0.17 g, 52%) was shown to be pure *trans*-4-methylbenzalacetophenone by comparison with an authentic sample. The crude reaction mixture was also analyzed by vpc. The analytical gas chromatography was performed on an Aerograph 350-B instrument with helium as the carrier gas on a column of Carbowax (20% on Chromosorb W) at 90°. Comparison of retention times and infrared spectra with those of known samples of toluene and benzaldehyde established the identity of the products. By employing benzonitrile as a suitable internal standard, a 40% yield of benzaldehyde and a 43% yield of toluene were found. Identical results were obtained when *cis*-1-benzyl-2-*p*-toluyl-3-phenylaziridine was treated with diphenyliodonium iodide in refluxing tetrahydrofuran.

Treatment of 1-Benzyl-2-benzoyl-3-phenylaziridine with Diphenyliodonium Iodide in Tetrahydrofuran.—A mixture of 0.63 g of *trans*-aziridine I and 0.82 g of diphenyliodonium iodide in 200 ml of tetrahydrofuran was refluxed for 72 hr. The solvent was removed by distillation and the dark yellow oil was chromatographed on a liquid-liquid partition column. The chromatogram consisted of three well-defined peaks with retention volumes of 1800, 2200, and 2680 ml. The first peak (0.51 g, 63%) was shown to be pure iodobenzene by comparison with an authentic sample. The second peak (45 mg) was identified as 2,5-diphenyloxazole. The last peak (310 mg) was shown to be *trans*-benzalacetophenone. Careful examination of the crude reaction mixture by vapor phase chromatography showed two additional compounds. The analytical gas chromatography was performed on a Aerograph A-90 instrument with helium as the carrier gas on a Carbowax column (20% on Chromosorb W) at 90°. Collection of these compounds and comparison with authentic samples of toluene and benzaldehyde established their identity. Comparable results were obtained when *cis*-1-benzyl-2-benzoyl-3-phenyl-

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(20) A. Padwa, *J. Amer. Chem. Soc.*, **87,** 4365 (1965).

(21) All melting points are corrected and boiling points are uncorrected. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark, and Alfred Bernhardt Laboratories, Hohenweg, Germany. The infrared absorption spectra were determined on a Perkin-Elmer Infracord spectrophotometer, Model 137. The ultraviolet absorption spectra were measured with a Cary recording spectrophotometer, using 1-cm matched cells. The nuclear magnetic resonance spectra were determined at 60 Mc with the Varian Associates high-resolution spectrophotometer. Tetramethylsilane was used as an internal standard.

aziridine was treated with diphenyliodonium iodide in refluxing tetrahydrofuran.

Reaction of 1-Cyclohexyl-2-benzoyl-3-phenylaziridine with Diphenyliodonium Iodide in Tetrahydrofuran.—A mixture of 0.61 g of *cis*-1-cyclohexyl-2-benzoyl-3-phenylaziridine (IV) and 0.82 g of diphenyliodonium iodide in 200 ml of tetrahydrofuran was allowed to reflux for 68 hr. The solvent was removed *in vacuo* to leave a dark yellow oil which was subjected to liquid–liquid partition chromatography. The chromatogram showed two major peaks with retention volumes of 1800 and 2700 ml of mobile phase. The first peak (518 mg, 64%) was identified as iodobenzene. The second peak (316 mg, 76%) was shown to be *trans*-benzalacetophenone. There was no detectable quantities of 2,5-diphenyloxazole found in the reaction mixture. Examination of the crude reaction mixture by vapor phase chromatography showed the presence of cyclohexanone (69%). The analytical gas chromatography was performed on an Aerograph A-90 instrument employing a Carbowax column (20% on Chromosorb W) at 50°. Similar results were obtained when *trans*-1-cyclohexyl-2-benzoyl-3-phenylaziridine was treated with diphenyliodonium iodide in refluxing tetrahydrofuran.

Treatment of 1-Cyclohexyl-2-*p*-toluyl-3-phenylaziridine with Diphenyliodonium Iodide in Tetrahydrofuran.—A mixture of 0.64 g of *cis*-1-cyclohexyl-2-*p*-toluyl-3-phenylaziridine (VIII) and 0.82 g of diphenyliodonium iodide in 200 ml of tetrahydrofuran was allowed to reflux for 76 hr. Evaporation of the solvent afforded a dark yellow oil which was subjected to liquid–liquid partition chromatography. The optical density trace showed two peaks with retention volumes of 1800 and 2800 ml of mobile phase. The first peak consisted of 496 mg (61%) of iodobenzene. The second peak contained 286 mg (67%) of *trans*-4-methylbenzalacetophenone. There was no detectable quantities of 2-phenyl-5-*p*-tolyloxazole found in the reation mixture. Analysis of the crude reaction mixture by gas chromatography confirmed the presence of cyclohexanone (59%). The analytical gas chromatography was performed on an Aerograph A-90 instrument using a SE-30 silicon column (20% on Chromosorb W) at 70°.

Decomposition of N-1-(2-Benzoyl-1-phenylethyl)cyclohexanimine with Diphenyliodonium Iodide.—N-1-(2-Benzoyl-1-phenylethyl)cyclohexanimine was prepared according to the procedure of Padwa and Hamilton.[15] A mixture of 0.31 g of N-1-(2-benzoyl-1-phenylethyl)cyclohexanimine and 0.41 g of diphenyliodonium iodide in 50 ml of tetrahydrofuran was allowed to reflux for 18 hr. The solvent was removed *in vacuo*, and the crude residue was analyzed by vapor phase chromatography on an Aerograph A-90 instrument. The products were separated on a column of Dow 710 silicone oil (0.2% on glass beads) at 170° at a flow rate of 50 cc/min. The material of retention time 6.2 min was collected in a Dry Ice trap connected to the gas outlet. The material obtained had an infrared spectrum and retention time identical with that of an authentic sample of *trans*-benzalacetophenone (78%). Analysis of the crude reaction mixture at 50° showed a major component with retention time of 2.3 min. Comparison of retention time and infrared spectra with that of an authentic sample of cyclohexanone established its identity. A sufficient quantity of water is present in the solvent to effect the conversion of the imine into ammonia and the carbonyl compound.

Preparation of α,β-Diphenyl-4-methylacrylophenone Oxide (IX).—A mixture of 59 g of benzyl-*p*-tolyl ketone and 40 g of benzaldehyde was saturated with hydrogen chloride gas at 0°. The solution was kept overnight and the solid material which formed was collected by filtration, washed thoroughly with 95% ethanol and ether, and dried to yield 100 g of 1-(4-methylphenyl)-2,3-diphenyl-3-chloro-propan-1-one. The chloride could be dehydrohalogenated to α,β-diphenyl-4-methylacrylophenone by refluxing a mixture of 60 g of the chloride, 40 g of fused sodium acetate, and 15.7 g of sodium carbonate in 240 ml of methanol for 3 hr. The solid which precipitated was collected by filtration, washed thoroughly with water, and dried to yield 55 g of α,β-diphenyl-4-methylacrylophenone. Recrystallization from ethanol gave a white crystalline solid, mp 105–106°. The infrared spectrum of the crystalline compound (KBr) is characterized by a carbonyl band at 6.06 μ. The nmr spectrum showed a singlet at τ 7.68 and a multiplet centered at 2.60. The peak areas were in the ratio of 1:5.

A solution of 30 g of the unsaturated ketone in 600 ml of methanol was treated with 60 ml of 30% hydrogen peroxide and 30 ml of 6 *N* aqueous sodium hydroxide. After the mixture had been stirred for 20 hr at room temperature, it was poured into 2 l. of water and extracted with ether. The ether extract was washed with water and dried over magnesium sulfate; the ether was removed. The residual α,β-diphenyl-4-methylacrylophenone oxide crystallized from 95% ethanol as white plates, mp 103–104°, to yield 17 g (60%). The infrared spectrum of this material showed a strong carbonyl band at 5.97 μ. The nmr spectrum showed a multiplet at τ 2.40 and singlets at 5.50 and 7.68. The peak areas were in the ratio of 14:1:3.

Anal. Calcd for $C_{22}H_{18}O_2$: C, 84.07; H, 5.73. Found: C, 83.89; H, 5.73.

Preparation of α-Tolyl-β-phenylacrylophenone Oxide (X).—The procedure of Kohler and Nygard was adapted to the present case.[22] A mixture of 15 g of 4′-methyldesoxybenzoin and 9.2 g of benzaldehyde was saturated with hydrogen chloride gas at 0° and was allowed to stand overnight at room temperature. The resulting solid was washed with 95% ethanol and dried to yield 18 g of β-chlorobenzal-4′-methyldesoxybenzoin. A solution of 10 g of the chloride, 7.0 g of fused potassium acetate, and 2.3 g of anhydrous sodium carbonate in 50 ml of methanol was boiled under reflux for 3 hr. The solid which precipitated was washed with water and collected by filtration to yield 6.8 g of α-tolyl-β-phenylacrylophenone. Recrystallization from ethanol gave crystals, mp 123–124°. The infrared spectrum (KBr) had a carbonyl band at 6.05 μ. The nmr spectrum in deuteriochloroform exhibited a multiplet centered at τ 2.40 and a singlet at 7.70.

A mixture of 5.0 g of α-tolyl-β-phenylacrylophenone, 20 ml of 30% hydrogen peroxide, 8.0 ml of 6 *N* sodium hydroxide, and 250 ml of methanol was stirred for 24 hr at room temperature. After the reaction mixture had been poured into water, the precipitated solid was recrystallized from 95% ethanol, mp 73–74°. The infrared spectrum exhibited a carbonyl band at 5.95 μ. The nmr spectrum consisted of a multiplet centered at τ 2.50 (14 H), a singlet at 5.50 (1 H), and a singlet at 7.92 (3 H).

Anal. Calcd for $C_{22}H_{18}O_2$: C, 84.08; H, 5.73. Found: C, 84.02; H, 5.83.

Preparation of α-Phenyl-β-tolylacrylophenone Oxide (XI).—Dry hydrogen chloride gas was passed through an ice-cooled mixture of 40 g of desoxybenzoin and 24 g of *p*-tolylaldehyde for 5 hr. The mixture was allowed to stand at room temperature for an additional 8 hr. The resulting solid was thoroughly washed with 95% ethanol and dried to yield 77 g of 1,2-diphenyl-3-*p*-tolyl-3-chloro-propan-1-one. The crude chloride could be dehydrohalogenated by refluxing a solution of 60 g of the chloride, 40 g of fused potassium acetate, and 16 g of anhydrous sodium carbonate in 250 ml of methanol for 48 hr. The solid which precipitated was collected by filtration, washed with water, and recrystallized once from 95% ethanol. The crude α-phenyl-β-tolylacrylophenone was used without further purification. A mixture of 5.0 g of the unsaturated ketone, 20 ml of 30% hydrogen peroxide, 8.0 ml of 6 *N* sodium hydroxide, and 250 ml of methanol was stirred for 48 hr at room temperature. After the reaction mixture had been poured onto water, the precipitated solid was recrystallized from 95% ethanol, mp 129–130°. The infrared spectrum exhibited a carbonyl band at 5.95 μ. The nmr consisted of a multiplet centered at τ 2.50 (14 H), a singlet at 5.50 (1 H), and a singlet at 8.80 (3 H).

Anal. Calcd for $C_{22}H_{18}O_2$: C, 84.08; H, 5.73. Found: C, 83.75; H, 5.76.

General Procedure for the Reaction of Substituted Acrylophenone Oxides with Diphenyliodonium Iodide.—All the reactions described were run under essentially the same experimental conditions and are illustrated by the following experiment with α,β-diphenyl-4-methylacrylophenone oxide (IX). A mixture of 0.5 g of IX and 0.5 g of diphenyliodonium iodide was heated in a sealed tube at 240° for 30 min. The resulting mixture was extracted with ether and the ethereal extracts were washed with 5% sodium bicarbonate solution and then with water. After the organic layer had been dried over sodium sulfate, the ether was removed and the impure material, dissolved in benzene, was chromatographed on a 2.5 × 91 cm column of silica gel, slurry packed in 3:1 benzene–hexane. The column was eluted with 9:1 benzene–hexane (2 l.) followed by benzene (1 l.). The eluent, in 50-ml fractions, was concentrated and dried *in vacuo*. The crystalline solid from elution with 9:1 benzene–hexane was identified as desoxybenzoin and that obtained from pure benzene was shown to be 4′-methyldesoxybenzoin.

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(22) E. P. Kohler and E. M. Nygard, *J. Amer. Chem. Soc.*, **52**, 4128 (1930).

The crude reaction mixture was also analyzed by vpc. The analytical gas chromatography was performed on a F & M Model 5720 instrument with helium as the carrier gas on a Carbowax 20M column (20% on Chromosorb P) at 240°. Comparison of retention times and infrared spectra with those of the authentic ketone and acid established the identity of the products. The results are recorded in Table II.

Registry No.—I, 6476-12-6; II, 6372-57-2; III, 2211-61-2; IV, 2211-65-6; V, 6476-13-7; VI, 6372-58-3; VII, 6372-29-8; VIII, 6476-39-7; IX, 15830-93-0; X, 15830-81-6; XI, 15856-59-4; XII, 15830-82-7; XIII, 15856-60-7; α,β-diphenyl-4-methylacrylophenone, 15830-83-8; α-tolyl-β-phenylacrylophenone, 15830-84-9; diphenyliodonium iodide, 2217-79-0; N-1-(2-benzoyl-1-phenylethyl)cyclohexanimine, 14802-27-8.

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Small Charged Rings. XI.[1] Synthesis and Reactions of 1,1,2,2-Tetrasubstituted Azetidinium Salts[2]

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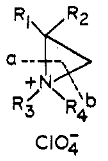
A convenient synthesis of 1,1,2,2-tetramethylazetidinium perchlorate (**2**) and 1-benzyl-1,2,2-trimethylazetidinium perchlorate (**3**) has been developed. The cyclization step in the sequence leading to these compounds involved treatment of γ-*sec*-aminoalkyl chlorides with silver perchlorate to afford the corresponding tertiary azetidine perchlorates in excellent yield. These were subsequently alkylated to give the quaternary azetidinium salts. 1,1-Dibenzyl-2,2-dimethylazetidinium perchlorate (**4**), as an intermediate, was found to undergo a facile eliminative ring opening in the presence of amines and could not be isolated. The structures of **2** and **3** have been verified by molecular weight determination and nmr spectroscopy. The tetramethyl salt **2** proved to be relatively unreactive, but the benzyltrimethyl salt **3** underwent solvolytic ring opening with alcohols to form N-(3-alkoxy-3-methylbutyl)-N-methylbenzylamine perchlorates. In the presence of sodium methoxide or upon heating in solution, both azetidinium salts exhibited a strong tendency to undergo eliminative ring opening to afford substituted 3-methyl-3-buten-1-ylamines. Azetidinium salt **3** combined with nitrones, specifically with substituted Δ^1-pyrroline-1-oxides, to afford 1:1 adducts containing the 2-oxa-1-aza-6-azoniabicyclo[5.3.0]decane ring system. This reaction is representative of a new type of ring expansion, expressed as ④$^+$ + 3 → ⑦$^+$, in which a four-membered charged ring combines with a 1,3-dipolar moiety to form a seven-membered charged ring. The structures of the adducts were established by cleavage of the 6,7 bond with lithium aluminum hydride, followed by cleavage of the 1,2 bond with zinc and acetic acid, accompanied by spectroscopic and chemical identification of the ultimate degradation products.

In the course of a continuing study of the reactions of 1,1,2,2-tetrasubstituted aziridinium salts (1), a number of facile ring openings and ring expansions have been observed.[4] In general, weak nucleophiles bring about ring opening at a so that SN1-type products are obtained,[5,6] while strong nucleophiles tend to approach the ring from the less hindered side in an SN2 manner to effect bond breaking at b.[7,8] Preliminary cleavage at a is also postulated as the initial step in the expansion of the aziridinium ring with aldehydes,[8] ketones,[9] and nitriles.[10] When both the 2 and the 3 position on the aziridinium ring are unsubstituted, more vigorous conditions are necessary for reaction to occur with nitriles.[11] These ring expansion reactions of aziridinium salts are codified within the general category ③$^+$ + 2 → ⑤$^+$, in which a charged, three-membered cycle is increased in size to a charged, five-membered cycle. The reaction of aziridinium salts with nitrones has introduced a new category: ③$^+$ + 3 → ⑥$^+$.[1] As a logical extension of this study, it was of interest to determine whether suitably substituted azetidinium rings could open and expand in a manner analogous to that of the more highly strained aziridinium system. Although a variety of azetidinium salts have been known for some time,[12,13] no extensive investigations into the chemistry of these charged four-membered heterocycles have been made until recently.[14-19]



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