

benzene and 160 mg. (1.59 mmoles) of triethylamine was added, rendering the solution homogeneous. A precipitate began to appear after 30 min. After 3 hr., triethylammonium *p*-nitrobenzenesulfonate began to crystallize; after 3 days crystals of dianilinium sulfate also separated. After 5 days, the benzene layer was decanted and the residue was washed with

benzene and dissolved in acetone. *N*-Phenylbenzenesulfonamide was not detected.

Acknowledgments. We are grateful to the National Science Foundation for support of this work under Grant GP 649. The n.m.r. spectrometer used was purchased with the aid of National Science Foundation Grant G-22689.

Epoxidation Studies. III. The Peracid Oxidation of Substituted Benzoylimines¹⁻³

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N,N-Dibenzoylamines have been identified as the major product of reaction of several monoarylimines of benzil with peracids. Data are presented demonstrating that 3-benzoyloxaziranes function as transient intermediates. The kinetics of the rearrangement of the relatively stable 2-cyclohexyl-3-phenyl-3-benzoyloxazirane to *N*-cyclohexyldibenzamide was studied. The rate was found to follow first-order kinetics. From these results we conclude that the mechanism of the rearrangement involves attack of the electron pair of nitrogen of the oxazirane ring on the neighboring benzoyl group. A study of the peracid epoxidation of the related class of *N*-benzoylimines was also carried out. It was found that substituted phenols and dibenzamide were the major products. A mechanism involving initial epoxidation is proposed to account for the results.

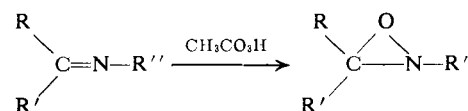
The oxidation of ketones to esters by means of peracids was first described in 1899 by Baeyer and Villiger⁴ and has proved useful in a variety of both synthetic and degradative studies. The early work has been reviewed in several places^{5,6} and a treatment of applications and experimental techniques is available.⁷ The application of this reaction to α,β -unsaturated ketones may lead either to cleavage toward or away from the carbon-carbon double bond. Still another possibility for this class of compounds is the preferential attack at the olefinic linkage leading to an α,β -epoxy ketone. Examples of the formation of all three types of compounds are available in the literature.^{8,9}

The epoxidation of the related class of benzoylimines has not yet been reported. The present investigation had its origin in our interest in determining which (if

either) type of behavior would be observed in this related reaction. In particular, we were interested in the possible stability of the unknown 2- and 3-benzoyloxaziranes. Such compounds are three-membered carbon-nitrogen-oxygen ring analogs of α,β -epoxy ketones. In view of the many polar rearrangements exhibited by the latter class of compounds, we considered that an investigation to determine whether 2- and 3-acyloxaziranes would undergo related transformations was desirable. In this paper we present evidence that shows still a third type of behavior is possible in the benzoylimine-peracid system.

Results and Discussion

The reaction initially examined was the treatment of monophenyl- (I) mono-*p*-methoxyphenyl- (II), and monocyclohexylbenzilimine (III) with anhydrous peracetic acid in methylene chloride. At the time, it was hoped that the reaction would proceed in a fashion analogous to the preparation of a wide variety of aliphatic oxaziranes.¹⁰ Emmons had previously demon-



strated that the conversion of imines to oxaziranes is a reasonably selective oxidation and may be carried out in the presence of functional groups which normally react with peracids.¹¹ It was hoped, furthermore, that the stability and reactivity of the oxazirane ring would be influenced by the benzoyl group present in the molecule.

The desired monoimines of benzil (I-III) were readily available from the corresponding amines on reaction with benzil at elevated temperatures. Yields of the benzoylimines prepared by this method were of the order of 75-85%.

Reaction of the monoanil of benzil¹² (I) with anhydrous peracetic acid in methylene chloride at 0° afforded in excellent yield a product whose structure was

(1) This work was presented in part at the 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965.

(2) For preliminary reports of this work see (a) A. Padwa, *Tetrahedron Letters*, No. 30, 2001 (1964); (b) *ibid.*, No. 14, 879 (1965).

(3) We gratefully acknowledge support of this research by the National Science Foundation (Grant GP-3972).

(4) A. V. Baeyer and V. Villiger, *Ber.*, 32, 3625 (1899).

(5) J. E. Leffler, *Chem. Rev.*, 45, 385 (1949).

(6) P. A. S. Smith, "Molecular Rearrangements," Part I, P. De Mayo, Ed., John Wiley and Sons, Inc., New York, N. Y., 1963, p. 577.

(7) C. H. Hassall, *Org. Reactions*, 9, 81 (1957).

(8) J. Boeseken and A. L. Soesman, *Rec. trav. chim.*, 52, 874 (1933).

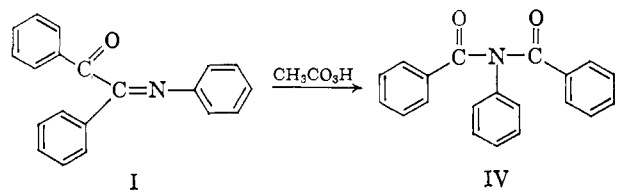
(9) E. Wenkert and M. Rubin, *Nature*, 170, 708 (1952).

(10) W. D. Emmons, *J. Am. Chem. Soc.*, 78, 6208 (1956).

(11) W. D. Emmons, *ibid.*, 79, 5739 (1957).

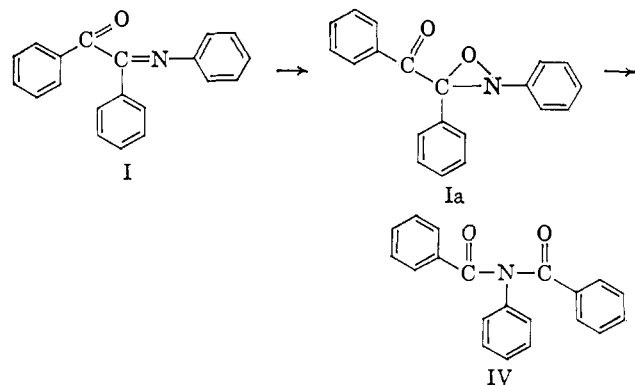
(12) J. Biltz, *Ann.*, 386, 224 (1909).

demonstrated to be *N,N*-dibenzoylaniline (IV). The assignment was supported by elemental analysis, spectroscopic data, and hydrolysis of the material with sulfuric acid in aqueous ethanol to give a quantitative yield of benzanilide and benzoic acid. Further verification was obtained by comparison with an authentic sample prepared by a procedure described by Freundler.¹³ The main reaction, therefore, proceeded according to the following equation.



Small amounts of benzanilide and benzoic acid were also found, probably arising from hydrolysis of IV during the work-up. Oxidation of I with *m*-chloroperbenzoic acid afforded an identical result.

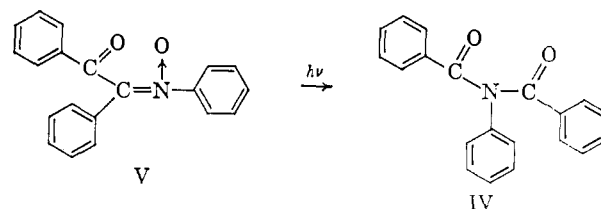
The formation of this product can be explained by postulating that an oxazirane intermediate is formed which subsequently rearranges to *N,N*-dibenzoylaniline. The stability of the oxazirane ring is known to



be markedly influenced by its substituent groups. Thus, efforts to prepare 2-phenyl- and 2-benzoyloxaziranes were unsuccessful because of the facile decomposition of the oxazirane after it was formed.¹¹ In the above case, the stability of the oxazirane ring is apparently markedly influenced by the substituent groups on the ring and may exist only as a transient intermediate. It was therefore considered desirable to prepare oxazirane Ia under nonacidic conditions. Observations in the literature of Beckmann-like rearrangements in nitrones suggests one such possibility¹⁴⁻¹⁶ Calvin and Splitter have reported that the initial product obtained from the irradiation of nitrones is an oxazirane.¹⁷ With this in mind we have examined the photolysis of *N*-phenylphenylbenzoylnitrone (V) in an attempt to generate the oxazirane under nonhydrolytic conditions.

Photolysis of *N*-phenylphenylbenzoylnitrone (V)¹⁸ in anhydrous ether or benzene with a Vycor filter for 24 hr. gave in almost quantitative yield an isomer to which structure IV is assigned.¹⁹ The photoproduct

can be isolated in pure form by evaporation of the solvent and recrystallization. The photochemical rear-



rangement of nitron V to *N,N*-dibenzoylaniline probably proceeds through the intermediacy of the oxazirane. A similar rearrangement has been previously reported by Krohnke who observed that the photolysis of benzoyl-*N*-(*p*-dimethylaminophenyl)nitron gave predominantly *N*-formyl-*N*-benzoyl-*p*-dimethylaminoaniline.²⁰ It was suggested that an acyloxazirane was initially formed and further rearranged to the observed product. The effect of the substituent groups of the oxazirane ring may be interpreted in (at least) two ways, decision between which is not presently possible. Either the substituent modifies the nature of the excited state, as observed in the photoreduction of substituted benzophenones,²¹ or else the substituent affects the stability of the oxazirane intermediate. The latter explanation seems quite plausible since oxazirane Ia, assumed to be formed from the peracid oxidation of the related benzoylimine, gave the same transformation product under nonphotochemical conditions.

The fact that oxazirane Ia is too unstable to be isolated by conventional techniques may be related to an earlier report by Emmons,¹¹ whose efforts to prepare *N*-phenyl-substituted oxaziranes were unsuccessful because of their instability. Similarly, the report that substituted *N*, α -diphenylnitrones when irradiated in solution gave rearranged products can best be explained by assuming oxaziranes as transient intermediates. By analogy with strained, small ring compounds, it is to be expected that the bond angle deformation present in the three-membered oxazirane ring would result in more *s*-character of the external bonds.^{22,23} Since a phenyl group is known to have electron-withdrawing properties, attachment of this group to the 2-position of the oxazirane could destabilize the ring system. Apparently, the destabilization factor is large enough to prohibit isolation of compound Ia. In order to test the validity of this hypothesis the reaction of compounds II and III with *m*-chloroperbenzoic acid was examined.

Epoxidation of monoimine II gave *N*-(*p*-methoxyphenyl)dibenzamide (VI) in better than 80% yield. The structure of VI was confirmed by its unequivocal synthesis from benzoyl chloride and *p*-anisidine. Again in the case of II, it is reasonable that an oxazirane is formed which subsequently rearranges. When the monocyclohexylimine of benzil (III) was treated with *m*-chloroperbenzoic acid, a 50% yield of 2-cyclohexyl-3-phenyl-3-benzoyloxazirane (VII) was obtained. The oxazirane structure of VII rests on the elemental

(13) M. P. Freundler, *Bull. Soc. Chim.*, [3] 31, 63 (1904).

(14) J. Splitter and M. Calvin, *J. Org. Chem.*, 20, 1086 (1955).

(15) F. Krohnke, *Ann.*, 604, 203 (1957).

(16) L. Chardonens and P. Heinrich, *Helv. Chim. Acta.*, 32, 656 (1949).

(17) J. Splitter and M. Calvin, *J. Org. Chem.*, 23, 651 (1958).

(18) F. Krohnke, *Ber.*, 72B, 534 (1939).

(19) M. L. Scheinbaum, *J. Org. Chem.*, 29, 2200 (1964), has also shown that *N,N*-dibenzoylaniline is formed from the photolysis of nitron V.

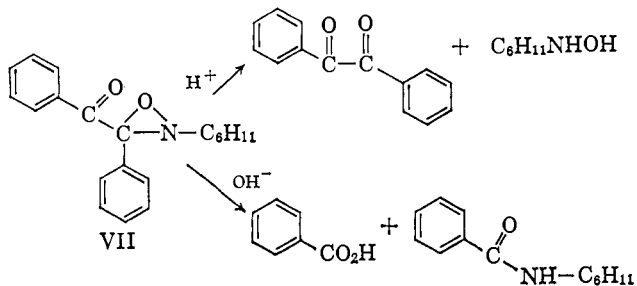
(20) F. Krohnke, *Ann.*, 604, 203 (1957).

(21) G. Porter and P. Suppan, *Proc. Chem. Soc.*, 191 (1964).

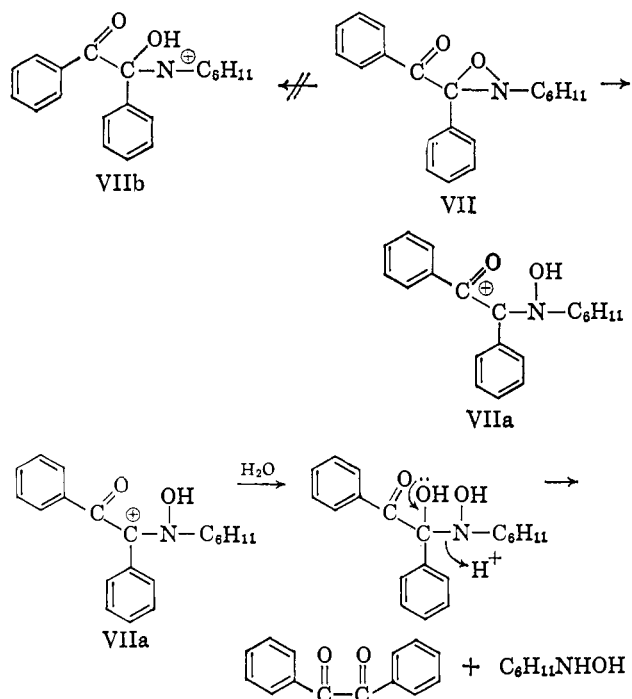
(22) C. A. Coulson and W. E. Moffit, *J. Chem. Phys.*, 15, 151 (1947).

(23) A. D. Walsh, *Trans. Faraday Soc.*, 45, 179 (1949).

analysis and on the basis of chemical and physical data cited below. The infrared spectrum of VII shows a strong carbonyl band at 5.94 and a sharp strong band at 6.91 μ characteristic of the oxazirane ring.¹¹ The material isolated was an active oxygen compound, and an analytical sample assayed iodometrically for 99.8% purity. The acid-catalyzed hydrolysis afforded benzil and cyclohexylhydroxylamine, whereas basic hydrolysis gave cyclohexylbenzamide and benzoic acid.



It is of interest to speculate at this point concerning the mechanism of the above hydrolyses. The products derived from the acid-catalyzed hydrolysis of VII can be rationalized by the assumption that the initial step in the hydrolysis involves protonation and cleavage of the oxazirane ring to leave a positive charge on the carbon α to the carbonyl group. The fission of the oxazirane ring to form transient cation VIIa rather than VIIb appears to be justified; the formation of structure VIIb would be expected to give products derived from phenyl or benzoyl migration as has been observed for a number of other oxaziranes.¹¹ No such products were detected from the hydrolysis of VII.

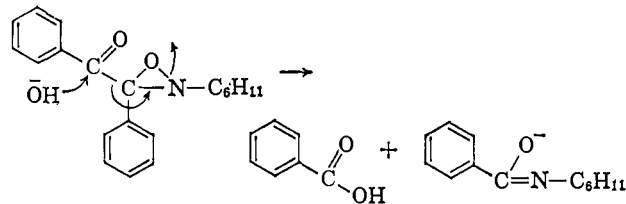


Although a carbonyl group is usually considered to destabilize an adjacent carbonium ion (such as VIIa),^{24,25} there is no evidence bearing on the extent

(24) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, p. 150.

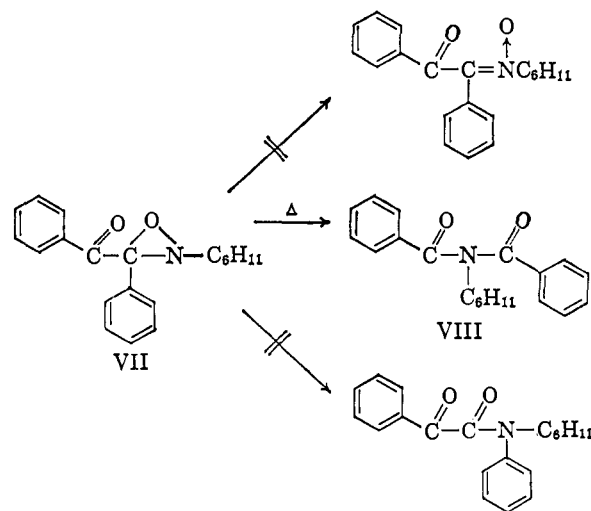
(25) The failure of certain α -halo ketones to react with silver nitrate has been attributed to such destabilization (for example, see R. L. Shriner, R. C. Fuson, and D. T. Curtin, "The Systematic Identification

of this destabilization relative to the stability of an electron-deficient nitrogen atom. The fact that N,N-dibenzoylcyclohexylamine was not obtained from the acid-catalyzed hydrolysis of VII supports the postulation that the rearrangement of 3-benzoyloxaziranes to N,N-dibenzylamines is purely pyrolytic in nature and is not acid catalyzed. The basic hydrolysis of VII can readily be explained by assuming attack of the base on the benzoyl group, as is shown below.



This is consistent with the findings that the oxazirane ring itself is not very reactive toward basic reagents.¹¹

Having established that a 3-benzoyloxazirane could be isolated, it became necessary to investigate its rearrangement. Previous reports by Emmons¹¹ have demonstrated that the thermal conversion of 3-phenyloxaziranes gave exclusively the corresponding nitrones. However, compound VII when refluxed in acetonitrile for 36 hr. was converted quantitatively to N-cyclo-



hexyldibenzamide (VIII). The proof of structure VIII rests on the elemental analysis, spectroscopic data, and hydrolysis to N-cyclohexylbenzamide and benzoic acid. Final verification was obtained by comparison with an authentic sample prepared from N-cyclohexylbenzamide and benzoylchloride. The isolation of VIII as opposed to the nitron adds credence to the supposition that oxazirane intermediates are involved in the epoxidation of benzoylimines and that such intermediates rearrange by a thermal process.

The rearrangement of 3-benzoyloxaziranes to N,N-dibenzylamines formally corresponds to migration of a benzoyl group from carbon to nitrogen with concurrent formation of a carbonyl bond. Perhaps in its simplest form it can be represented by heterolytic cleavage of the oxazirane followed by benzoyl migration. The zwitterionic intermediate bears a strong resemblance to the intermediate involved in the pinacol

of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 143).

rearrangement. The results obtained, suggesting the preferential migration of a benzoyl group, are not without precedent. The decarbonylation of diphenyl triketone was found to be explained most readily if the migration of a benzoyl group was assumed.²⁶ As has been pointed out by House,²⁷ there is no inherent reason why the migration of an acyl group should not be comparable with the migration of an aryl group. The exclusive shift of the benzoyl group is consistent with the hypothesis that the electron pair available on the neighboring nitrogen of the oxazirane ring provides the driving force for selective benzoyl migration. Examination of the reaction kinetics of the thermal rearrangement of VII to VIII supports this conclusion.

It was possible to conduct the rearrangement of VII to VIII in solution in acetonitrile and to follow the kinetics of the reaction by determining the decrease in the active oxygen content of the oxazirane. The rearrangement followed first-order kinetics; the rates at three temperatures are shown in Figure 1 and typical data for the rearrangement at 373.3°K. in Table I

Table I. Rearrangement of VII to VIII in Acetonitrile at 373.3°K.

Time, hr.	Sample, mg.	Sodium thio-sulfate (0.05 N), ml.	Initial concn. of VII, moles/l. $\times 10^4$	Final concn. of VII, moles/l. $\times 10^4$	Unrear., %
0	122.1	15.93	3.98	3.98	100.0
2	137.6	13.49	4.48	3.38	75.4
4	129.0	9.24	4.21	2.31	54.9
6	131.5	6.52	4.29	1.63	38.1
8	134.8	4.46	4.39	1.13	25.4
10	118.3	2.71	3.86	0.675	17.5
12	140.5	2.18	4.57	0.545	11.9

(see Experimental Section). The activation energy for the rearrangement of VII was determined from the dependence of the first-order rate constants on temperature (Figure 2). The observed value of ΔE^* , 21.7 kcal./mole, was obtained; calculation of the entropy of activation (ΔS^*) (Table II) showed that it was un-

Table II. First-Order Rate Constants and Entropies of Activation for the Rearrangement of VII to VIII

Rate run no.	Temp., °K.	$k_1 \times 10^6$, sec. ⁻¹	ΔH^* , kcal.	ΔS^* , e.u.
1	373.3	5.26	21.2	-22.0
2	360.8	1.79	21.2	-22.2
3	348.3	0.647	21.2	-21.8

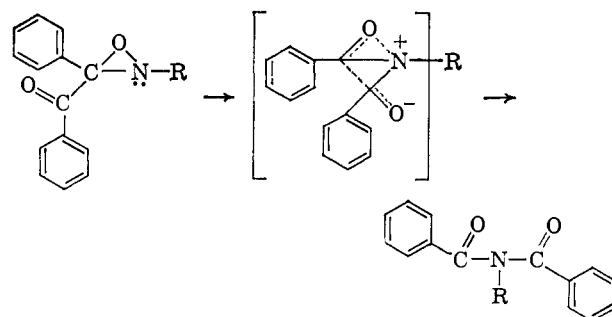
usually large for a first-order reaction (-22.0 e.u.) and was negative. The large negative entropy of activation can be explained in two ways. Attack by the electron pair localized on nitrogen at the benzoyl group in the activated complex would certainly result in a decrease in the number of degrees of freedom, thereby resulting in a negative entropy of activation. To the extent that the electron pair becomes involved in

(26) J. D. Roberts, D. R. Smith, and C. C. Lee, *J. Am. Chem. Soc.*, **73**, 618 (1951).

(27) H. O. House and D. J. Reif, *ibid.*, **77**, 6525 (1955).

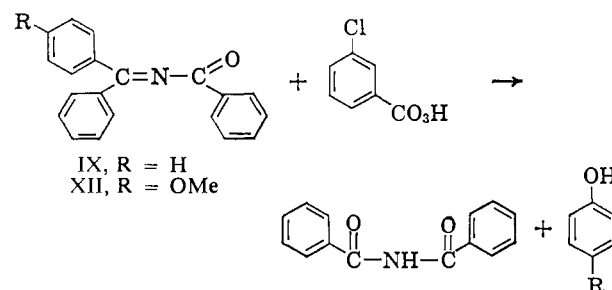
bonding with the benzoyl group, the transition state becomes more highly solvated and results in a more rigid solvated structure than starting material.

The fact that the rearrangement of VII to VIII follows first-order kinetics provides evidence that the reaction is intramolecular. The transition state for the migration of a benzoyl group could be likened to the formation of an analog of a bicyclo[1.1.0]butane, in which the benzoyl group becomes attached to nitrogen at virtually the same time that it is detached from



carbon. It is evident that the relief of strain of the three-membered oxazirane ring provides the driving force for the rearrangement.

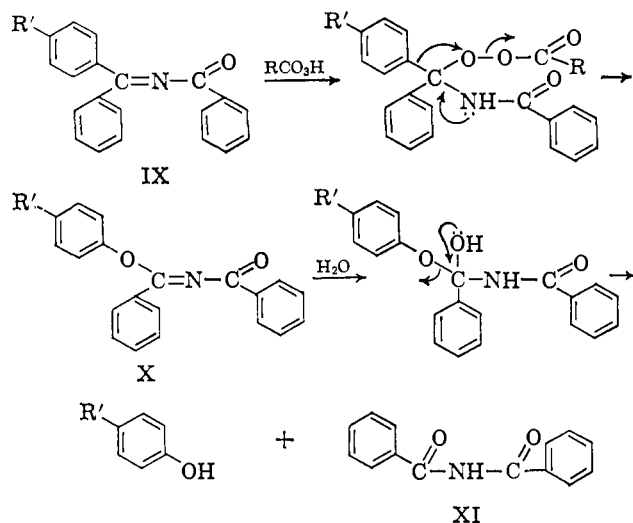
Evidence having been presented supporting an oxazirane intermediate in the peracid epoxidation of carbon-substituted benzoylimines, it became of interest to consider the epoxidation of the related class of N-benzoylimines. N-Diphenylmethylenbenzamide (IX) was chosen for the initial study. A convenient, one-step synthesis of N-diphenylmethylenbenzamide has previously been reported in the literature by Exner.²⁸ When a mixture of IX and *m*-chloroperbenzoic acid was refluxed for 1 hr. in 1,2-dichloroethane, a reddish orange solution was formed. Work-up of the residue, after removal of solvent, showed that dibenzamide (67%) and phenol (58%) were the major products of the reaction. The main reaction, therefore, proceeded according to the following equation.



This result may be rationalized by a number of different schemes. One possibility involves addition of peracid to the double bond giving an α -benzamido peroxy ester. This species can then undergo a peroxide rearrangement of a well-recognized type, migration occurring either concerted with O-O bond heterolysis, or subsequent to it, to give an aryl-N-benzoylbenzimidate (X), which under work-up conditions hydrolyzed to dibenzamide (XI) and phenol.²⁹⁻³¹

(28) O. Exner, *Chem. Listy*, **50**, 779 (1956).

(29) Another mechanistic possibility involves initial formation of a 2-benzoyloxazirane followed by its subsequent rearrangement to X. The driving force for the rearranging step is presumably the relief of strain in the oxazirane ring. Although we are unaware of any close analogy, recent work by Sheehan on the thermal conversion of the rela-



Evidence that migration from carbon to oxygen contributes significantly to the transition state is found in the peracid oxidation of *N*-(*p*-methoxy- α -phenylbenzylidene)benzamide (XII). Compound XII was prepared by treating the Grignard reagent of *p*-bromoanisole with benzonitrile at 0° for 10 min., followed by the addition of a slight excess of benzoyl chloride. Removal of the solvent after normal work-up conditions gave an excellent yield of the desired *N*-benzoylimine. Treatment of XII with *m*-chloroper-

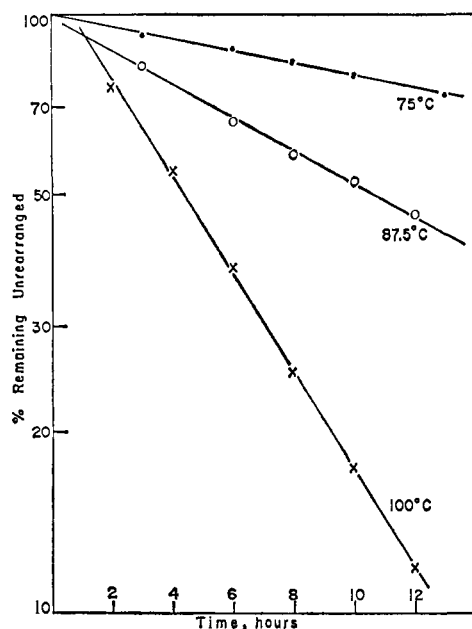


Figure 1. Rate of rearrangement of 2-cyclohexyl-3-phenyl-3-benzoyloxazirane to *N,N*-dibenzoylcyclohexylamine.

benzoic acid in 1,2-dichloroethane afforded dibenzamide (X, 63%) and *p*-methoxyphenol (57%). Careful examination of the residue revealed no detectable amounts of *N*-benzoyl-*p*-methoxybenzamide and phenol. The order of preference for migration of *p*-methoxy-

tively stable α -lactam, 1-*t*-butyl-3,3-pentamethyleneaziridone, to an isomeric oxirane bears similar characteristics.³⁰

(30) J. C. Sheehan and I. Lengyel, *J. Am. Chem. Soc.*, **86**, 746 (1964).

(31) We wish to thank Professor P. A. S. Smith for bringing this possibility to our attention.

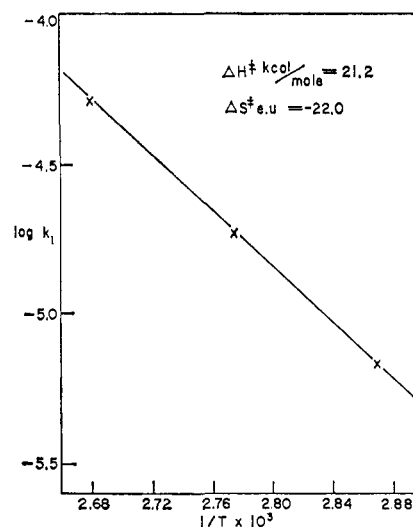


Figure 2. Dependence of the first-order rate constant k_1 on temperature for the rearrangement.

phenyl > phenyl is that expected for a reaction in which the rearrangement is a concerted process. It shows the same relative mobilities as have been observed in other migrations to an electron-deficient atom.³² The group that migrates preferentially is the one best able to sustain a positive charge in the transition state.

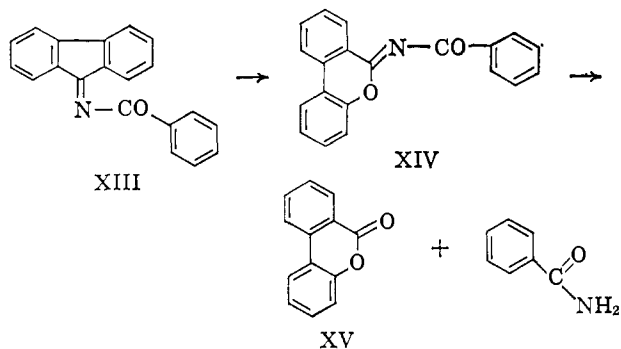
In an attempt to ascertain the reality of an aryl-*N*-benzoylbenzimidate intermediate (XI), a mixture of *N*-diphenylmethylenebenzamide (IX) and *m*-chloroperbenzoic acid in 1,2-dichloroethane was heated in a sealed tube for 1 hr. at 250°. The close resemblance of the proposed intermediate XI to an arylimido ester, which is known to undergo thermal rearrangement to an arylated diphenylamine, prompted this attempt.³³ It was felt that, since the Chapman rearrangement is a general phenomena for a large number of aryl imido esters,³⁴ this would provide additional evidence for the intermediacy of XI. Experimentally, pyrolysis of such a mixture afforded mainly dibenzamide and phenol without any detectable formation of *N,N*-dibenzoylaniline (IV). Thus it seems that if intermediate XI is produced from the epoxidation of the *N*-benzoylimine (IX) it does not give the product characteristic of the Chapman rearrangement. Failure to detect *N,N*-dibenzoylaniline (IV) as a product from the thermolysis of the crude reaction mixture described above does not necessarily reject XI as an intermediate in the epoxidation of *N*-benzoylimines. Since the mechanism of the Chapman rearrangement involves attack of the electron pair of the nitrogen on the migrating group, the absence of rearrangement in this case may be due to the electron-withdrawing benzoyl group which markedly retards the reaction.

Confirming evidence that the aryl-*N*-benzoylbenzimidate XI is formed at an intermediate stage is found however in the behavior of *N*-fluoren-9-ylidenebenzamide (XIII) with peracid. In this case hydrolysis of the intermediate *N*-benzoyl-2'-hydroxy-2'-biphenyl-2'-carboximidic acid δ -lactone (XIV) gave 2-hydroxy-

(32) Reference 6, p. 585.

(33) A. W. Chapman, *J. Chem. Soc.*, 1992 (1925).

(34) J. W. Schulenberg and S. Archer, *Org. Reactions*, **14**, 1 (1965).



diphenyl-2'-carboxylic acid lactone (XV) and benzamide. All attempts to isolate intermediate XIV prior to hydrolysis have failed presumably due to the facile hydrolysis of compounds of this structure. The isolation of lactone XV and benzamide strongly suggests the presence of an aryl-N-benzoylbenzimidate intermediate, which upon hydrolysis gave products different from those observed in the acyclic case but which are totally compatible with an intermediate such as XIV.

Experimental Section³⁵

Preparation of the Monoanil of Benzil (I). Benzil (42 g.) was heated with 20 g. of aniline at 150° for 2 hr. The mixture was cooled and 75 ml. of 95% ethanol was added. The yellow crystalline solid which precipitated was separated and dried to give 54 g. (81%), m.p. 98–103°. Recrystallization from ethanol afforded material of m.p. 105–106°. ¹²

Preparation of Monoimine II. A mixture of benzil (10.5 g.), *p*-anisidine (12.3 g.), and 0.1 ml. of concentrated hydrochloric acid was heated for 45 min. at 170°. The mixture was allowed to cool and 50 ml. of 95% ethanol was added. The solid was separated and dried to give 19.6 g. (85%), m.p. 120–124°. Recrystallization of the crude solid from ethanol gave material which melted at 125–126°.

Anal. Calcd. for C₂₁H₁₇NO₂: C, 79.98; H, 5.43; N, 4.44. Found: C, 79.91; H, 5.50; N, 4.54.

The infrared spectrum of monoimine II shows bands at 6.01 (conjugated carbonyl) and 6.18 μ (carbon-nitrogen double bond). ³⁶

Preparation of the Monocyclohexylimine of Benzil (III). A mixture of 21 g. of benzil and 10 g. of cyclohexylamine was heated at 180° for 1 hr. Upon cooling and diluting with 75 ml. of 95% ethanol, a white, crystalline solid precipitated. This material was filtered and dried to give 24 g. (76%) m.p. 55–70°. Recrystallization of the solid gave a white, crystalline solid which melted at 75–76°.

Anal. Calcd. for C₂₀H₂₁NO: C, 82.44; H, 7.26; N, 5.49. Found: C, 82.58; H, 7.21; N, 5.53.

The infrared spectrum of the imine was chiefly characterized by a sharp, intense carbonyl band at 5.96 and a strong carbon-nitrogen double bond at 6.14 μ . The ultraviolet spectrum in 95% ethanol had a maximum at 250 m μ (ϵ 27,000). A 2,4-dinitrophenyl-

(35) Melting points were determined on a Fisher-Johns micro hot stage, unless otherwise specified, and are uncorrected. Analytical samples were dried at 50° *in vacuo* unless otherwise specified. Infrared spectra were calibrated against a polystyrene film.

(36) See L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons., Inc., New York, N. Y., 1958: (a) Chapter 9; (b) Chapter 15.

hydrazone derivative melted at 186–187° after repeated crystallization from ethanol-ethyl acetate.

Reaction of I with Anhydrous Peracetic Acid. The procedure of Emmons¹¹ was adapted to the present case. To 20 ml. of methylene chloride with vigorous stirring and cooling in an ice bath was added 0.5 ml. of 90% hydrogen peroxide and 2 drops of sulfuric acid. Acetic anhydride (2.24 g.) was then added dropwise to the cooled solution over a 15-min. period. The mixture was subsequently stirred for 15 min. in the ice bath and for 30 min. at room temperature. The clear solution of peracetic acid so obtained was then added dropwise over a 20-min. period to a solution of 5.0 g. of the monoanil of benzil in 30 ml. of methylene chloride stirred in an ice bath. After addition, the ice was allowed to melt and the mixture was allowed to stand overnight at room temperature. It was then washed with 60 ml. of water, two 100-ml. portions of cold 15% aqueous ammonia, and finally 50 ml. of 10% sulfuric acid. The organic extract was dried over magnesium sulfate, and evaporation of the solvent left 4.52 g. of a clear oil. Recrystallization from ethanol gave crystals, m.p. 165–166°.

Anal. Calcd. for C₂₀H₁₅NO₂: C, 79.71; H, 5.02; N, 4.65. Found: C, 79.68; H, 5.01; N, 4.59.

The material was identified by comparison with a known sample of dibenzanilide prepared by a procedure described by Freundler.¹³ The yield of dibenzanilide was 89%.

Irradiation of *N*-Phenylphenylbenzoylnitrone (V). *N*-Phenylphenylbenzoylnitrone (V), m.p. 157°, was prepared by the procedure of Krohnke.¹⁸ A solution of 3.0 g. of nitrone V in 1 l. of anhydrous ether was irradiated with an internal, water-cooled mercury arc lamp (Hanovia, Type L-450 w.) with a Vycor filter. Purified nitrogen was passed through the solution for at least 45 min. before irradiation commenced, and a positive pressure of nitrogen was maintained throughout. The photolysis was followed by withdrawing small samples at fixed intervals without interrupting the system. The samples were analyzed by thin layer chromatography. After 24 hr., 95% of the starting material had disappeared and a new spot had appeared in its place. After the irradiation was completed, the solution was evaporated to dryness to give a solid, m.p. 158–161°. The compound was identified as dibenzanilide by its infrared spectrum and undepressed mixture melting points. Similar results were obtained when the photolysis of V was carried out in methanol, benzene, carbon tetrachloride, and aqueous dioxane solutions.

Reactions of Monoimine II with *m*-Chloroperbenzoic Acid. To 5.0 g. of monoimine II in 50 ml. of methylene chloride was added 3.11 g. of *m*-chloroperbenzoic acid. There was slight warming on addition. The mixture was stirred for 12 hr. at room temperature. The solution was extracted with four 50-ml. portions of 10% sodium carbonate and washed once with water. The organic layer was dried over magnesium sulfate, and evaporation left 4.1 g. (81%) of a solid, m.p. 138–144°. Recrystallization from ethanol gave white crystalline material, m.p. 145–146°. The material analyzed for *N*-(*p*-methoxyphenyl)dibenzamide.

Anal. Calcd. for C₂₁H₁₇NO₃: C, 76.12; H, 5.17; N, 4.23. Found: C, 75.94; H, 5.24; N, 4.20.

The infrared spectrum of this material in a potassium bromide pellet had bands at 5.91 and 6.02 μ in accord with its assignment as a dibenzoylamide. The material was identical in spectral and melting point properties with an authentic sample prepared by heating 1 g. of N-(*p*-methoxyphenyl)benzamide with 1 g. of benzoyl chloride in the presence of 5 ml. of pyridine for 2 hr. on a steam bath.

m-Chloroperbenzoic Acid Oxidation of the Monocyclohexylimine of Benzil (III). To an ice-cold solution of 6 g. of III in 100 ml. of methylene chloride was added 4.1 g. of *m*-chloroperbenzoic acid. The cold solution was stirred for 3 hr. at 0–5° and for 10 hr. at room temperature. Removal of most of the solvent *in vacuo* was followed by addition of ether (300 ml.) and extraction with four 50-ml. portions of 10% sodium carbonate. The ethereal solution was dried over sodium sulfate. Evaporation of the ether left 6.2 g. of a yellow oil. The impure material, dissolved in benzene, was chromatographed on a 2.5 × 91 cm. column of silica gel (Davison silica gel, grade 950, 6–200 mesh) slurry packed in benzene. The column was eluted with 1 l. of 1% ethyl acetate–benzene, 500 ml. of 5% ethyl acetate–benzene, and 1 l. of 10% ethyl acetate–benzene. The eluent, in 50-ml. fractions, was concentrated and dried *in vacuo*. The crystalline solid from elution with benzene (0.72 g., 12%) was identified as benzil by comparison with an authentic sample.

On further elution with 1% ethyl acetate–benzene, 3.8 g. (51%) of a white crystalline solid, m.p. 104–107°, was obtained. This material was assigned structure VII, 2-cyclohexyl-3-phenyl-3-benzoyloxazirane, on the basis of chemical and physical data cited below. Recrystallization of the crude solid afforded crystals, m.p. 108–109°.

Anal. Calcd. for C₂₀H₂₁NO₂: C, 78.14; H, 6.89; N, 4.56. Found: C, 78.38; H, 6.95; N, 4.54.

The infrared showed a strong carbonyl band at 5.94 μ . The ultraviolet spectrum in 95% ethanol had a maximum at 253 m μ (ϵ 10,000). The n.m.r. spectrum had a multiplet at τ 2.42 and a broad band at τ 8.45. The peak areas were in the ratio of 1.0:1.1. An active oxygen assay on this compound showed 99.9% purity.³⁷

Acid-catalyzed hydrolysis of oxazirane VII was achieved by refluxing 300 mg. of VII in 5 ml. of 95% ethanol (containing 0.1 ml. of sulfuric acid) for 12 hr. The ethanol was removed *in vacuo* and the residue was taken up in ether. The ethereal solution was extracted once with 10% sodium carbonate and dried over sodium sulfate. Evaporation of the ether and drying left 180 mg. of benzil. The aqueous solution was acidified to pH 3 and was continuously extracted with ether for 2 days. The ether layer was dried over magnesium sulfate, and evaporation of the solvent left 110 mg. of a solid, m.p. 140°, which was identified as cyclohexylhydroxylamine by comparison with an authentic sample prepared according to the procedure of Feuer and Vincent.³⁸

Basic hydrolysis of oxazirane VII was achieved by treating VII (150 mg.) with 60 mg. of potassium hy-

druide in 5 ml. of methanol and allowing the solution to sit at room temperature for 48 hr. The basic solution was diluted with 20 ml. of water followed by ether extraction. The ethereal solution was dried over sodium sulfate. Evaporation of the solvent left 82 mg. of a solid, identified as N-cyclohexylbenzamide. The basic aqueous layer was acidified to pH 3 with 10% hydrochloric acid and extracted with ether. Evaporation of the ether left 62 mg. of benzoic acid, m.p. 120–121°.

With 5% ethyl acetate–benzene as the eluent, 1.3 g. (21%) of N-cyclohexyldibenzamide (VIII) was obtained. Recrystallization from ethanol afforded white crystals, m.p. 132–133°.

Anal. Calcd. for C₂₀H₂₁NO₂: C, 78.14; H, 6.89; N, 4.56. Found: C 78.32; H, 6.95; N, 4.53.

The infrared spectrum had sharp carbonyl bands at 5.88 and 6.05 μ . The ultraviolet spectrum in 95% ethanol had a λ_{\max} 253 m μ (ϵ 11,000). Acid-catalyzed hydrolysis of this compound gave N-cyclohexylbenzamide and benzoic acid.

Elution with 10% ethyl acetate–benzene afforded 1.05 g. of N-cyclohexylbenzamide. The compound was identified by its infrared spectrum and comparison with a known sample. Further elution with more polar solvents afforded intractable material.

Rearrangement of 2-Cyclohexyl-3-phenyl-3-benzoyloxazirane to N,N-Dibenzoylcyclohexylamine. A 0.10-g. sample of the oxazirane (VII) was sealed in an evacuated tube and heated at 200° for 0.5 hr. The resulting oil was crystallized from ethanol and yielded 0.095 g. (95%) of the N,N-dibenzoylcyclohexylamine (VIII), m.p. 132–133°.

The following procedure was used in determining the kinetics of the rearrangement of VII to VIII. A solution was prepared containing approximately 6% by weight of VII in acetonitrile (dried over phosphorus pentoxide and redistilled). The solution was sealed in ampoules made from 8-mm. Pyrex tubing, which were then placed in a large thermostated oil bath. At definite time intervals tubes were removed and immediately cooled in Dry Ice–acetone. The tubes were then opened and the solutions were diluted with 30 ml. of glacial acetic acid and 20 ml. of distilled water. The active oxygen content was determined iodometrically by adding 2 ml. of a saturated potassium iodide solution and titrating the liberated iodine with 0.05 *N* sodium thiosulfate solution. The concentrations of the oxazirane (VII) could be calculated from its remaining titre. The per cent rearrangement was determined by comparing the concentrations of VII determined by this analytical method with the concentrations calculated for the solutions assuming that no rearrangement had occurred. The analytical method was shown to be accurate to within less than 2%. Temperature control was maintained with 0.1°, and the thermometers employed were calibrated against one certified by the Bureau of Standards. The data for a typical run are presented in Table I. In this run, the acetonitrile solution contained 6.105% by weight of VII.

The first-order rate constants for the rearrangement of VII as a function of temperature are listed in Table II, and the rates at three temperatures are shown graphically in Figure 1. The activation energy was determined to be 21.7 kcal./mole from a plot of log k_1 against 1/ T (Figure 2), using the equation ΔE^*

(37) Active oxygen assays on this compound were determined using potassium iodide and acetic acid according to the procedure of Siggia, "Qualitative Organic Analyses via Functional Groups," John Wiley and Sons., Inc., New York, N. Y., 1949, p. 100.

(38) H. Feuer and B. F. Vincent, *J. Am. Chem. Soc.*, **84**, 3771 (1962).

= $-4.58 \times \text{slope}$. The enthalpy of activation was determined from a plot of $\log k_1/T$ against $1/T$. The entropies of activation were calculated from the equation of $\Delta F^* = -2.3RT(\log k_1/T - \log K'/h)$ where $R = 1.987 \text{ cal./}^\circ\text{K.}$, $K' = \text{Boltzmann constant} = 1.3805 \times 10^{-16} \text{ erg/}^\circ\text{K.}$, $h = \text{Planck constant} = 6.624 \times 10^{-23} \text{ erg. sec.}$

The product was isolated from one rearrangement of VII under the conditions of the kinetic runs to make sure that the reaction formed VIII in the presence of acetonitrile as solvent. A solution of 0.1236 g. of VII in dry acetonitrile (2.0 ml.) was placed in a tube, which was sealed and heated for 15 hr. at 373.3°K. The tube was cooled and the solvent was removed under reduced pressure. The partially crystalline oil which separated was recrystallized from ethanol. The yield of VIII obtained as two crops was 0.108 g. (82%), which after recrystallization from ethanol melted at $132\text{--}133^\circ$ and did not depress the melting point of an authentic sample of VIII.³⁹

Reaction of *N*-Diphenylmethylenbenzamide (IX) with *m*-Chloroperbenzoic Acid. *N*-Diphenylmethylenbenzamide (IX), m.p. $116\text{--}117^\circ$, was prepared by the procedure of Exner.²⁸ A solution of 4 g. of IX and 2.74 g. of *m*-chloroperbenzoic acid in 100 ml. of 1,2-dichloroethane was refluxed for 1 hr. After this time no more active oxygen content remained as evidenced by the lack of iodine liberation from an acidic potassium iodide solution. The solution was extracted with four 50-ml. portions of 10% sodium hydroxide and washed once with water. The organic layer was dried over magnesium sulfate, and evaporation left 2.96 g. of an oil. Recrystallization from ethanol afforded 2.21 g. of a solid, m.p. $150\text{--}151^\circ$. The material was identified as dibenzamide by comparison with a known sample. The yield of dibenzamide was 67%. The aqueous extracts were acidified to pH 3 and continuously extracted with ether for 3 days. The ethereal solution was dried over magnesium sulfate, and evaporation of the solvent left 0.76 g. (58%) of phenol, identical with an authentic sample.

Preparation of *N*-(*p*-Methoxy- α -phenylbenzylidene)-benzamide (XII). To 3.6 g. of magnesium metal in 300 ml. of anhydrous ether and 25 g. of *p*-bromoanisole was added, during 10 min. at 0° , a solution of 12.7 g. of benzonitrile in 30 ml. of ether. The mixture was refluxed for 15 min. and treated with 16 g. of benzoyl chloride in 30 ml. of ether during 15 min. at room temperature. After boiling an additional 10 min., the mixture was decomposed with 60 g. of ammonium chloride in 250 ml. of water. The ethereal layer was washed once with water and dried over sodium sulfate. Evaporation of the solvent left a crystalline solid, m.p. $106\text{--}109^\circ$. Recrystallization from ethanol gave white crystalline material, m.p. $109\text{--}110^\circ$.

Anal. Calcd. for $\text{C}_{21}\text{H}_{17}\text{NO}_2$: C, 79.98; H, 5.43; N, 4.44. Found: C, 80.36; H, 5.66; N, 4.40.

The infrared spectrum had bands at 6.01, 6.21, and 8.01μ . The ultraviolet spectrum in 95% ethanol had λ_{max} 229 $m\mu$ (ϵ 17,700), 250 (15,600), 285 (15,600),

and 297 (15,000). The n.m.r. spectrum in deuteriochloroform showed a multiplet centered at τ 2.72 and a singlet at 6.29. The integrated peak areas were in the ratio of 4.7:1.

***m*-Chloroperbenzoic Acid Epoxidation of XII.** Following the general procedure previously outlined, 2 g. of *N*-(*p*-methoxy- α -phenylbenzylidene)benzamide and 3.48 g. of *m*-chloroperbenzoic acid were refluxed for 2 hr. in 100 ml. of 1,2-dichloroethane. The solution was extracted with four 50-ml. portions of 10% sodium hydroxide and washed once with water. The organic layer was dried over sodium sulfate, and evaporation left 1.38 g. of a solid. Recrystallization from ethanol afforded 1.06 g. (63%) of dibenzamide, m.p. $150\text{--}151^\circ$. The aqueous extracts were acidified to pH 3 and continuously extracted with ether for 3 days. The ethereal solution was dried over magnesium sulfate, and evaporation of the solvent left 0.42 g. of *p*-methoxyphenol (57%). The neutral residue has an infrared spectrum that was very similar to that of dibenzamide.

Preparation of *N*-Fluoren-9-ylidenebenzamide (XIII). 9-Fluorenonimine,⁴⁰ m.p. $124\text{--}125^\circ$, was prepared by the procedure of Harris, Harriman, and Wheeler. A mixture of 2 g. of 9-fluorenonimine and 2.51 g. of benzoic anhydride in 50 ml. of benzene was heated under reflux for 5 hr. The cooled solution was washed with two 50-ml. portions of 10% sodium carbonate and once with water. The organic layer was dried over magnesium sulfate, and evaporation left 3.6 g. of a solid, m.p. $124\text{--}127^\circ$. Recrystallization from 95% ethanol afforded a yellow crystalline compound, m.p. $127\text{--}128^\circ$.

Anal. Calcd. for $\text{C}_{20}\text{H}_{15}\text{NO}$: C, 84.78; H, 4.63; N, 4.94. Found: C, 84.88; H, 4.92; N, 4.92.

The infrared spectrum had bands at 6.03, 6.29, and 8.01μ . The n.m.r. spectrum shows only aromatic hydrogens centered at τ 2.66.

Reaction of *N*-Fluoren-9-ylidenebenzamide (XIII) with *m*-Chloroperbenzoic Acid. A mixture of 2.0 g. of XIII and 6.2 g. of *m*-chloroperbenzoic acid in 100 ml. of 1,2-dichloroethane was heated to reflux for 1 hr. Upon cooling, the organic solution was extracted with four 50-ml. portions of 10% sodium carbonate and dried over sodium sulfate. Evaporation of the solvent left 1.92 g. of a yellow oil which was chromatographed on a column of Florisil. The first fractions obtained with 1% ethyl acetate-benzene gave 0.61 g. of a white solid, m.p. $84\text{--}87^\circ$. Recrystallization from ethanol afforded a crystalline solid, m.p. $91\text{--}92^\circ$. The structure of this product was shown to be 2-hydroxyphenyl-2'-carboxylic acid lactone (XV) by comparison with a known sample prepared according to the procedure of Doering and Speers.⁴¹ On further elution with 10% ethyl acetate-benzene, 0.94 g. (54%) of benzamide was obtained. The compound was identical with a known sample of benzamide by mixture melting point and infrared spectral comparison. Further elution afforded intractable material.

(40) G. H. Harris, B. R. Harriman, and K. W. Wheeler, *J. Am. Chem. Soc.*, **68**, 846 (1946).

(41) W. von E. Doering and L. Speers, *ibid.*, **72**, 5515 (1950).

(39) An authentic sample of VIII was prepared by heating 700 mg. of *N*-cyclohexylbenzamide with 700 mg. of benzoyl chloride in 3 ml. of pyridine for 2 hr. on a steam bath.