

3-BENZOYLOXAZIRANES; A NEW REARRANGEMENT TO  
SUBSTITUTED N,N-DIACYLAMINES

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Although oxaziranes have received considerable attention, there exists no authenticated preparation of a 3-acyloxazirane<sup>1,2,3</sup> (II). Such compounds are three-membered carbon-nitrogen-oxygen ring analogs of  $\alpha, \beta$ -epoxyketones. In view of the many polar rearrangements exhibited by the latter class of compounds, it became of interest to determine whether 3-acyloxaziranes would undergo related transformations.

Treatment of the mono-anil of benzil (Ia) with meta-chloroperbenzoic acid or anhydrous peracetic acid in methylene chloride afforded in excellent yield a product

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<sup>1</sup> W. D. Emmons, J. Am. Chem. Soc., 78, 6208 (1956);  
79, 5739 (1957).

<sup>2</sup> J. Splitter and M. Calvin, J. Org. Chem., 23, 651 (1958).

<sup>3</sup> The numbering of the oxazirane ring has been designated as  $\text{}^3\text{C}-\overset{\text{O}}{\text{N}}_2$  i. e. see reference No. 1.



by Emmons,<sup>1</sup> whose efforts to prepare 2-phenyl and 2-benzyl-oxaziranes were unsuccessful because of their instability. Similarly Calvin and Splitter<sup>2</sup> have reported that substituted N,  $\alpha$ -diphenyl nitrones when irradiated in solution gave products that 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.<sup>5</sup> 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 IIa. In order to test the validity of this hypothesis the reaction of compounds Ib and Ic with meta-chloroperbenzoic acid was examined.

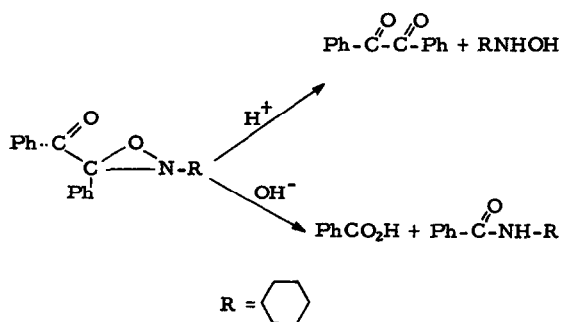
Mono-imine Ib (m. p. 125-126<sup>o</sup>) was prepared by condensation of equivalent molar quantities of benzil and p-anisidine.<sup>6</sup> Epoxidation of Ib gave N-(p-methoxyphenyl)-

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<sup>5</sup> C. A. Coulson and W. E. Moffit, J. Chem. Phys., 15, 151 (1947); A. D. Walsh, Trans. Faraday Soc., 45, 179 (1949).

<sup>6</sup> Satisfactory carbon, hydrogen and nitrogen analyses were obtained for all the new compounds described herein.

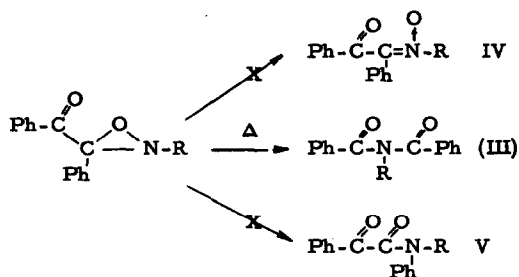
dibenzamide (IIIb) in better than 90% yield. The structure of IIIb was confirmed by its unequivocal synthesis from benzoyl chloride and *p*-anisidine. Again in the case of Ib, it is reasonable that an oxazirane is formed which subsequently rearranges. When the mono-cyclohexylimine of benzil (Ic) was treated with meta-chloroperbenzoic acid a 60% yield of 2-cyclohexyl-3-phenyl-3-benzoyloxazirane (IIIc) (m. p. 108-109°) was obtained. The oxazirane structure of IIIc is based on elemental analysis, spectroscopic data, hydrolysis to benzil and cyclohexylhydroxyl amine, and basic hydrolysis to cyclohexylbenzamide and benzoic acid.



In addition, the material isolated was an active oxygen compound, and an analytical sample assayed iodometrically for 99.8% purity. The order of stability of these

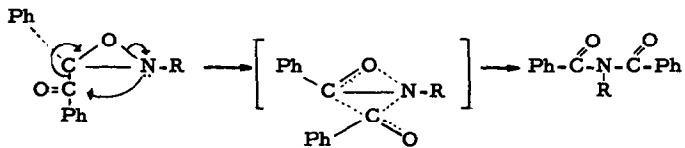
oxaziranes seems therefore to be a function of the electronic properties of the substituent at the 2-position of the ring.

Having established that a 3-benzoyloxazirane could be isolated it became necessary to investigate its rearrangement. Previous reports by Emmons<sup>1</sup> have demonstrated that the thermal conversion of 3-phenyloxaziranes gave exclusively the corresponding nitrones. However, compound IIc when refluxed in acetonitrile for 12 hours was converted quantitatively to N-cyclohexyl-dibenzamide (IIIc).



The isolation of IIIc as opposed to the nitrone (IV) adds credence to the supposition that oxazirane intermediates are involved in epoxidation of benzoylimines.

Consideration of a possible transition state which might be involved in the isomerization suggests that benzoyl migration might be attributed to formation of a bond between the carbonyl group and the electron pair located on nitrogen.



The existence of such neighboring group participation in the transition state would certainly favor benzoyl migration.

Further study of the scope, mechanism and utility of rearrangement of such oxaziranes are in progress.

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