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OXIDATION OF 3-CHLORO-3-PHENYLDIAZIRINE BY m-CHLOROPEROXYBENZOIC ACID

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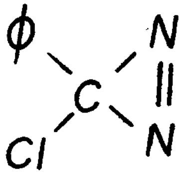
The chemistry of diazirines has been characterized by the facile thermal decomposition to generate carbenes[1-3], their ease of reduction and general low reactivity as compared with the linear isomers[4]. The oxidation of reactive diazirines by ozone has been reported[5], but the direct oxidation on the nitrogen-nitrogen double bond of this system is not known. We wish to report the results of the oxidation of 3-chloro-3-phenyldiazirine, 1[6], by m-chloroperoxybenzoic acid. It was hoped that the unknown azoxy analogs 2 could be produced.



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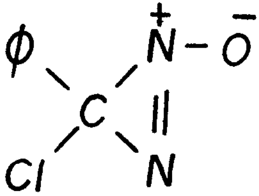

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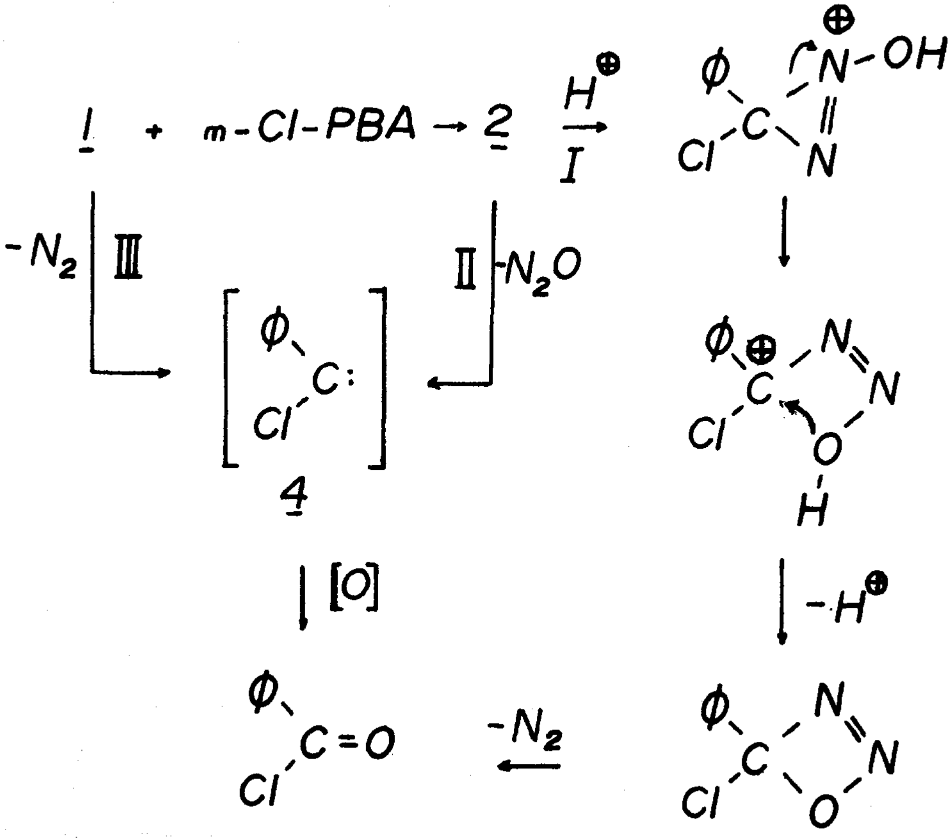
The reaction was carried out by refluxing 1 with equimolar or excess of m-chloroperoxybenzoic acid (85%, Aldrich) in chloroform at 61°C for five hours. The reaction was very slow at room temperature. On cooling, the resulting solution was worked up quickly under basic conditions. Chromatographic analysis of the products indicated the presence of benzoyl chloride (45-50%), benzaldehyde (about 40%), trace amounts of 1 and benzoic acid; and a significant amount of bis(m-chlorobenzoyl)peroxide[7]. The components were identified by comparing their ir and tlc with the authentic samples. Benzoyl chloride was converted to benzamide, m.p.130° and benzaldehyde to its 2,4-dinitrophenylhydrazone, m.p. 237°.

The formation of benzaldehyde was attributed to the decomposition of unreacted starting material upon aquous work-up. Padwa and Eastman[8] have also noted the presence of benzaldehyde when the thermolysis of 1 was carried out in alcoholic solvents.

The formation of benzoyl chloride can be rationalized by the following pathways:



3

Pathway I suggests that the N-oxide is being generated but decomposes under the conditions of the reaction. This mechanism is substantiated by the work of Snyder et al[9] on the oxidation of diazobasketene with m-chloroperoxybenzoic acid to give the N-oxide which rearranged readily in boron trifluoride etherate. It is noted that in pathway I the formation of 1,2,3-oxadiazete, 3, does not have to involve the protonation step; the N-oxide 2 could give 3 directly. An alternative pathway, II, would be for 2 to expel nitrous oxide to generate a carbene 4 which could then be oxidized to benzoyl chloride[10]. However, this pathway was ruled unlikely since nitrous oxide was not detected in our experiment. For pathway III, the mechanism would involve the intermediate formation of a carbene 4 which could then be oxidised to product. If a carbene is an intermediate, as in pathways II and III, one would expect products resulting from the insertion of carbene into the solvent molecule (chloroform) but this is not observed. In similar attempts to oxidise 3,3-pentamethylenediazirine with m-chloroperoxybenzoic acid, the only product was cyclohexanone. If the carbene mechanism is involved in this case, cyclohexene (resulting from 1,2-hydrogen shift of the carbene) should be among the products[11]. This was not found. In view of the above evidence, we have reason to believe that pathway I is the most probable although compound 3 has not been isolated.

Further investigation on diazirine oxidation is in progress.

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REFERENCES

1. H. M. Frey and I. D. R. Stevens, J. Am. Chem. Soc 84, 2647 (1962).
2. M. T. H. Liu and K. Toriyama, J. Phy. Chem 76, 797 (1972).
3. M. T. H. Liu and K. Toriyama, Can. J. Chem 51, 2393 (1973).
4. E. Schmitz, " Advances in Heterocyclic Chemistry (A.R. Katritzky ed.)", Academic Press, New York, pp 126-130, vol 2, 1963.
5. E. Schmitz and C. Hörig, Chem. Ber 100, 2101 (1967).
6. W. H. Graham, J. Am. Chem. Soc 87, 4396 (1965).
7. In a blank reaction without 3-chloro-3-phenyldiazirine, the same amount of m-chloroperoxybenzoic acid (85% Aldrich) was used and treated under identical experimental conditions. The same amount of bis(m-chlorobenzoyl)-peroxide was recovered.
8. A. Padwa and D. Eastman, J. Org. Chem., 34, 2728 (1969).
9. J. P. Snyder, L. Lee and D. G. Farnum, J. Am. Chem. Soc 93, 3816 (1971).
10. Analogous oxidation of carbenes by dimethyl sulfoxide has been reported by R. Oda, M. Mieno and Y. Hayaski, Tetrahedron Lett. 2363 (1967).
11. H. M. Frey and A. W. Scaplhorn, J. Chem. Soc (A), 968 (1966).