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EPOXIDATION STUDIES OF N-DIARYLMETHYLENE-BENZAMIDES

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Although the background and evidence for the oxidation of α,β-unsaturated ketones with peracids, particularly as regards formation of epoxyketones and esters, have been reviewed[1], the epoxidation of the related class of N-dialkylmethylene-amides has not yet been reported. Therefore, it was of interest to us to determine 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-benzoyloxazirane. Our study has shown that still a third type of behavior is possible in the N-diarylmethylene-benzamide-peracid system.

When a mixture of N-diphenylmethylene-benzamide(I) (3.70 mmoles, obtained via the procedure of Exner[2]) and meta-chloroperbenzoic acid (4.07 mmoles) was refluxed for one hour in 1,2-dichloroethane, a reddish orange solution was formed. Workup of the residue, after removal

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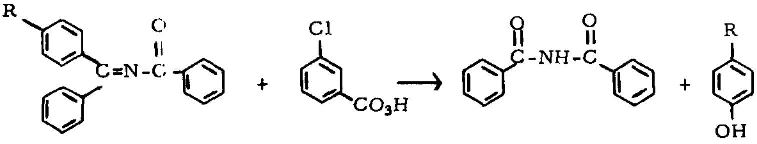
1) C. H. Hassall, "Organic Reactions", Vol. IX, R. Adams, Ed., John Wiley and Sons, Inc., New York, N. Y., 1957, p. 81.

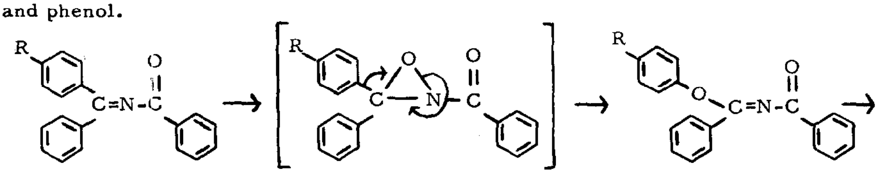
2) O. Exner, Chem. Listy, 50, 779 (1956).

of solvent, showed that dibenzamide (67%) and phenol (58%) were the major products of the reaction[3]. The main reaction, therefore, proceeded according to the following equation:



R = H(I)
R = OMe(II)

This result may be rationalized by a number of different schemes. One possibility involves initial formation of a 2-benzoylоxazirane (III), followed by its subsequent rearrangement to an aryl-N-benzoylbenzimidate(IV), which under workup conditions hydrolyzed to dibenzamide and phenol.



III IV

The order of stability of oxaziranes has previously been demonstrated to be a function of the electronic properties of the substituent at the 2-position of the ring[4]. Attachment of the electron-withdrawing benzoyl group on the nitrogen apparently destablizes the ring and prohibits isolation of compound III The driving force for the rearranging step is

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[3] Dibenzamide and phenol were identified by comparison of IR and mixed melting points with that of an authentic sample.

[4] A. Padwa, Tetrahedron Letters, No. 30, 2001 (1964).

presumably the relief of an unfavorable electronic effect[5]. Although we are unaware of any close analogy, recent work by Sheehan[6] on the thermal conversion of the relatively stable α-lactam, 1-t-butyl-3, 3-pentamethyleneaziridone, to an isomeric oxirane bears similar characteristics.

Another mechanistic possibility[7] is that the oxazirane ring is never formed at all, due to the destabilization mentioned. Instead, an open-chain, dipolar precursor might undergo rearrangement directly without ring closure. This possibility has the advantage of simplicity, for it does not require the formation of an O-N bond that is only to be cleaved again. Furthermore, the reaction may actually proceed via addition of peracid to the double bond, giving an α-benzamido peroxy ester, which then can undergo a peroxide rearrangement of a well recognized type, migration occurring either concerted with O-O bond heterolysis, or subsequent to it.

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(II). Compound II was prepared by treating the Grignard reagent of p-bromoanisole with benzonitrile at 0° for ten minutes, followed by the addition of a

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5) Two reasonable alternative mechanisms involve N-O bond homolysis followed by an aryl to oxygen migration, or protonation of the transient 2-benzoyloxazirane with m-chlorobenzoic acid. Both mechanisms are consistent with the above data and on the basis of the results at this stage of the investigation one can not distinguish the three possibilities. The concerted mechanism has been used for simplicity.

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

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

slight excess of benzoyl chloride. Removal of the solvent after normal workup conditions gave a crystalline solid, m.p. 109-110°C[8]. Treatment of II with meta-chloroperbenzoic acid in 1,2-dichloroethane afforded dibenzamide (63%) and p-methoxy-phenol (57%). Careful examination of the residue revealed no detectable amounts of N-benzoyl-p-methoxy-benzamide and phenol. The order of preference for migration p-methoxy-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[9]. The group that migrates preferentially is the one best able to sustain a positive charge in the transition state.

Confirming evidence that the aryl-N-benzoylbenzimidate(IV) is formed at an intermediate stage is found in the behavior of N-fluoren-9-ylidene-benzamide(V) with peracid. In this case hydrolysis of the intermediate N-benzoyl-2'-hydroxy-2-biphenyl-2'-carboximidic acid δ-lactone(VI) gave 2-hydroxy-diphenyl-2'-carboxylic acid lactone[10] (VII) (46%) and benzamide (54%). All attempts to isolate the intermediate prior to hydrolysis have failed, presumably due to the facile

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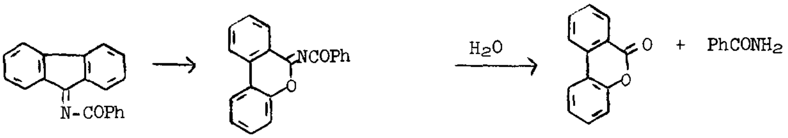
8) Satisfactory carbon, hydrogen and nitrogen analyses were obtained for all the new compounds described herein.

9) P. A. S. Smith, "Molecular Rearrangements", Part I, P. DeMayo, Ed., John Wiley and Sons, Inc., New York, N. Y., 1963, p. 585.

10) The product isolated was identical in all respects to an authentic sample prepared by the procedure of W. von E. Doering and L. Speers, J. Am. Chem. Soc., 72, 5515 (1950).

hydrolysis of compounds of this structure[11].



V VI VII

A consequence of such a mechanism as outlined above is that the group migrating from carbon to oxygen should do so intramolecularly and with retention of configuration when the point of attachment is a center of optical symmetry. Experiments designed to investigate this point and further study of the scope, mechanism and utility of epoxidation of related N-dialkylmethylene-amides are in progress.

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[11] In contrast to the peracid epoxidation of N-diarylmethylene-benzamides treatment of compounds I, II, and V with 10% sodium hydroxide and 30% hydrogen peroxide in methyl alcohol readily gave rise to the corresponding ketone and benzoic acid.