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THE REACTION OF QUINOLINE-1-OXIDES WITH *N*-PHENYLBENZIMIDOYL CHLORIDE

R. A. Abramovitch and R. B. Rogers

Department of Chemistry, University of Alabama,

University, Alabama 35486

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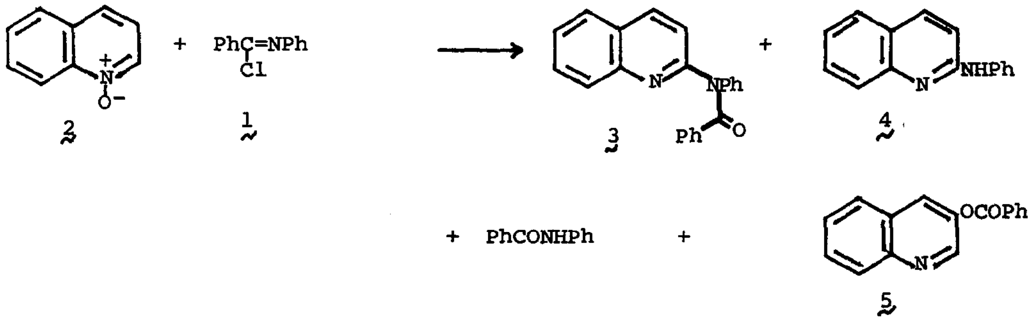
As an extension of our studies on the direct amination and acylamination of heteroaromatic *N*-oxides[1] we have examined the reaction of *N*-phenylbenzimidoyl chloride (**1**) with quinoline-1-oxide (**2**) and its 4-nitro derivative and obtained some unusual data which we now report.[2]

When **1** and anhydrous **2** were heated in 1,2-dichloroethane the following products were isolated[3] *prior to hydrolysis*: 2-(*N*-benzoylanilino)quinoline (**3**) (27.8%), 2-anilinoquinoline (**4**) (35.8%), benzanilide (17.8%), and 3-quinolyl benzoate (**5**) (33.5%), m.p. 61-62°.

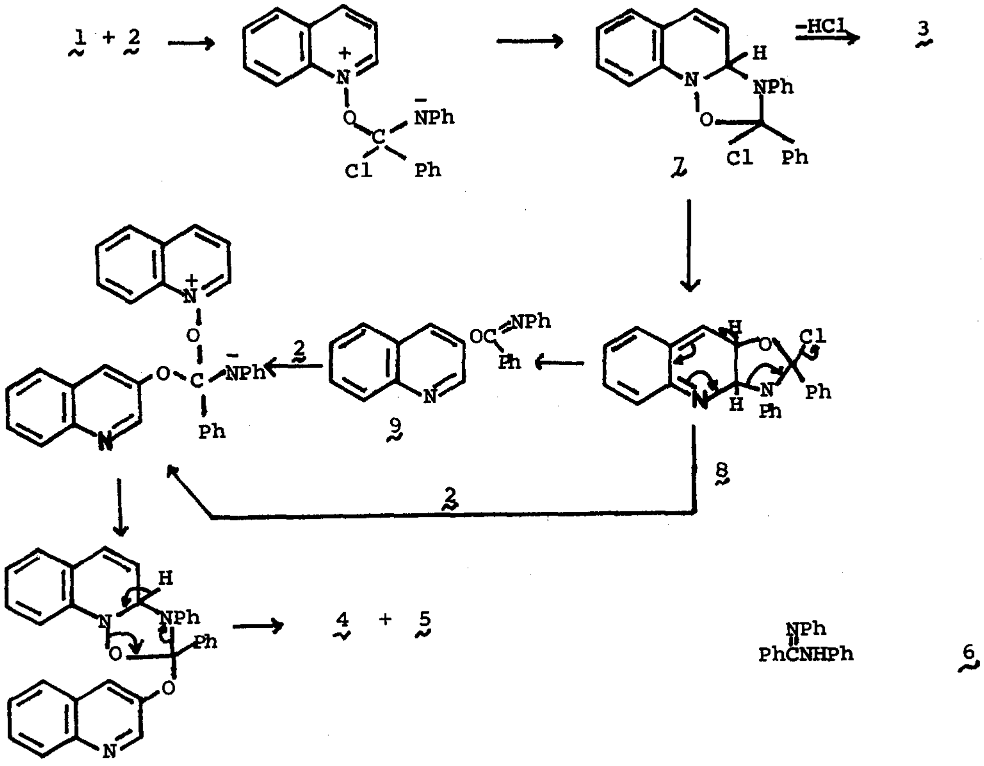


All the products were characterized by infrared, n.m.r. and mass spectrometry, and by elemental analysis as required, and authentic samples of each were prepared. 5 was also hydrolyzed to 3-hydroxyquinoline.

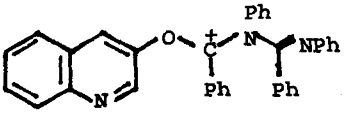
Interestingly, 4, which is formed in an amount almost equal to that of 5, appears directly as the reaction proceeds[4] and is not a product of hydrolysis. No benzoic acid was isolated under these conditions.

Reaction of 2 with *N*-phenylbenzonitrilium hexachloroantimonate did not proceed as satisfactorily and gave 3 (5%), benzanilide (25%), 5 (20%), and *N*,*N*'-diphenylbenzamidine (6) (10%),[5] m.p. 147-148° (n.m.r. and mass spectrum). No 2-anilinoquinoline (4) could be detected under these conditions.

A possible route to 5 from 1 which would account for its formation in the absence of any oxygen donor other than 2, and for the simultaneous formation of 4, is the following in which a 1,5-sigmatropic shift (7→8) is postulated:



In an attempt to verify this pathway, 9 [m.p. 113-115°, $\nu_{C=N}$ 1660 cm^{-1} M^+ m/e 324] was synthesized from the sodium salt of 3-hydroxyquinoline and N-phenylbenzimidoyl chloride in ethanol, and treated with 2 or 2-hydrochloride. In no case was any of the ester 5 isolated. On the other hand, we have found that reaction of 2,6-lutidine-1-oxide with 1 gave a complex mixture from which both 3-chloro-2,6-lutidine and O-(2,6-dimethyl-3-pyridyl)-N-phenylbenzimidate were isolated. The latter was characterized by its mass spectrum and by hydrolysis to 3-hydroxy-2,6-lutidine. The same imidate has been obtained by Parham and Sloan,[2] who also obtained the corresponding imidate from 2,4-dimethylquinoline-1-oxide. Formation of 6 when the benzonitrilium salt is used could proceed from 8 or 9 to a species such as 10, or perhaps from the nitrilium salt and benzanilide.



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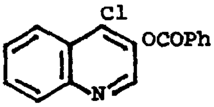

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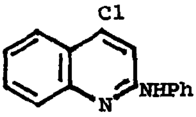

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The reaction of 4-nitroquinoline-1-oxide with 1 gives a large number of products of which only four have been identified: benzanilide, 4-chloro-3-quinolyl benzoate (11),[6] m.p. 115-116°, 4-chloroquinoline-1-oxide, and an oily mixture which could not be resolved, but which on boiling with 4N HCl gave 4-chloroquinoline-1-oxide, 4-chloro-3-hydroxyquinoline (also obtained by hydrolysis of 11) and 2-anilino-4-chloroquinoline (12),[8] m.p. 161-162°, together with polymeric material. The mode of formation of these products and the mechanism by which 5 is produced are under study.

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REFERENCES

(1) R. A. Abramovitch and G. M. Singer, *J. Amer. Chem. Soc.*, **91**, 5672 (1969).

(2) W. E. Parham and K. B. Sloan (in press, this journal). We thank Professor W. E. Parham for agreeing to the simultaneous publication of our results and his.

(3) Yields were determined by gas chromatographic analysis using a 20% SE-30 on Gas Chrom Q column.

(4) Its formation could be monitored by gas chromatography and it could be isolated either by g.l.c. or by column chromatography on silica gel using a 9:1 mixture of light petroleum (b.p. 60-110°): acetone as eluant. Amide **3** was stable under these conditions.

(5) Lit. m.p. 145-146°. G. Garcia Munoz, M. Lora Tamayo and R. Madronero, *Anales Real Soc. Espan. Fis. y Quim.*, **57B**, 465 (1961); *Chem. Abstr.*, **57**, 8496b (1962).

(6) The same product was isolated in low yield (4.3%) from the reaction of **2** with *N*-1-adamantylbenzonitrilium bromopentachloroantimonate.[7] $\nu_{C=O}$ 1745 cm^{-1}, n.m.r. (CDCl$_3$)δ8.81 (s, 1H, H-2), 8.56 (d, 1H, $J_{7,8}$ = 8Hz, H-8), 8.30-7.25 (m, 8H, aromatic H). That the $C_{(2)}$-H proton was a sharp singlet indicated that C-3 and C-4 were both substituted (**5** exhibits a $C_{(2)}$-H doublet, $J_{2,4}$ = 3Hz).

(7) R. A. Abramovitch and G. M. Singer, unpublished results.

(8) Lit. m.p. 161°. W. Dymek and Z. Zborowska, *Rocz. Chem.*, **38**, 925 (1964).