PHOTOLYSIS AND THERMOLYSIS OF QUINOLYL AND ISOQUINOLYL AZIDES IN ETHANETHIOL

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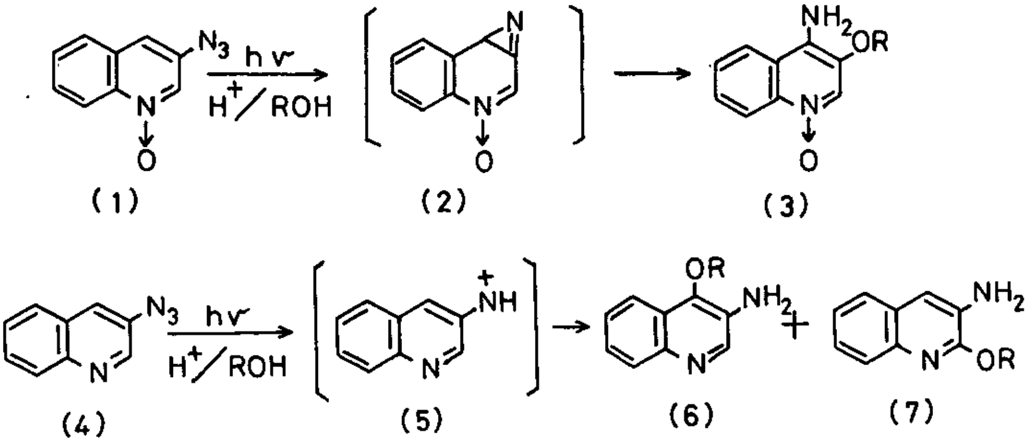
Abstract —— 3-Quinolyl azides (**8**), upon either irradiation or heating in ethanethiol, gave 3-amino-4-ethylthioquinolines (**9**), presumably *via* a radical process. Similarly, 4-isoquinolyl azides (**11**) gave 3-ethylthio- (**12**) and/or 1-ethylthio-4-aminoisoquinolines (**13**), and 8-quinolyl azide (**17**) gave 7-ethylthio- (**18**) and 5-ethylthio-8-aminoquinoline (**19**), while 4-quinolyl azides (**15**) gave only 8-aminoquinolines (**16**).

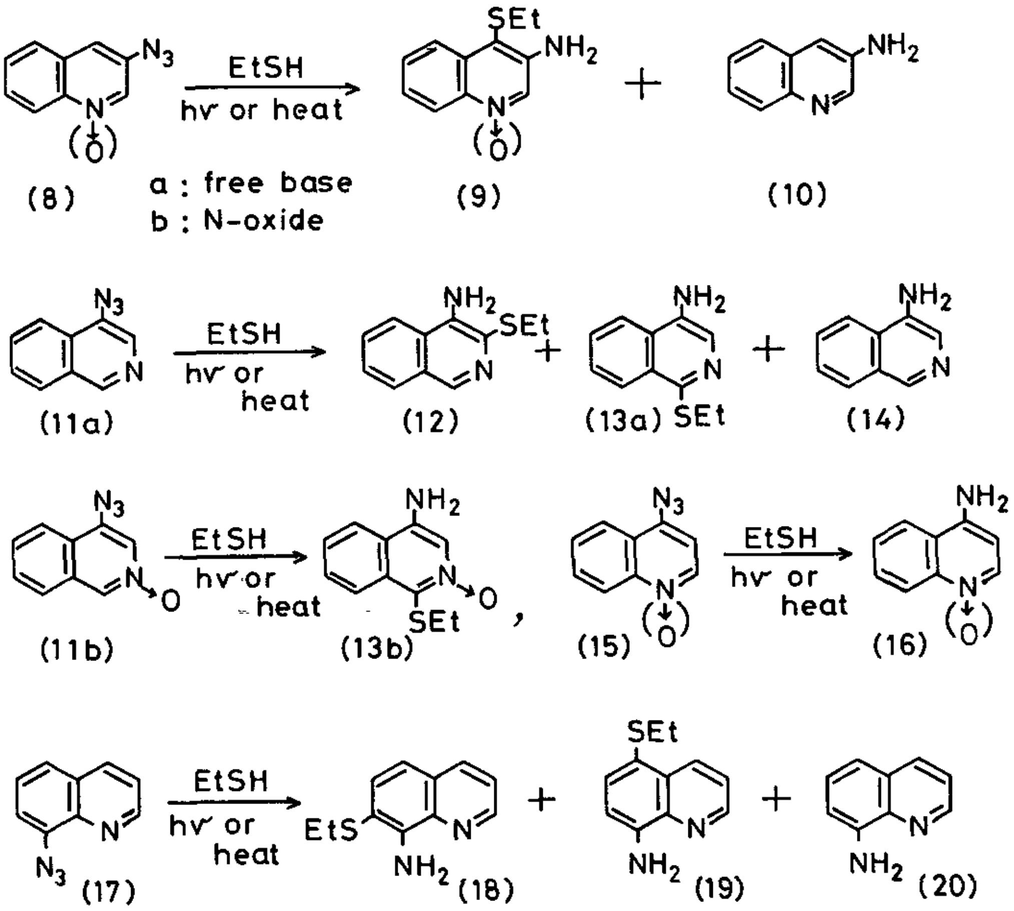
It is well documented that photolysis of aryl azides in the presence of bases gives ring-expansion products and/or ortho-substituted amino compounds *via* azirine intermediates.[1,2] Recently, we carried out the photolysis of pyridyl, quinolyl, and isoquinolyl azides under acidic conditions, and found that the other reaction, involving a nitrenium ion intermediate, also occurs in some cases to give γ-substituted amino compounds.[3,4] For example, 3-azidoquinoline N-oxide (**1**), upon



Scheme 1

irradiation in alcohols containing sulfuric acid, gave 3-alkoxy-4-aminoquinoline N-oxide (3) *via* the azirine intermediate (2), but the photolysis of 3-quinolyl azide (4) under the same conditions afforded 4-alkoxy- (6) and 2-alkoxy-3-aminoquinoline (7) *via* the nitrenium ion (5), as shown in Scheme 1.[4] As a continuation of these studies, we investigated the title reactions.

Photolytic[5] and thermal decomposition of 3-quinolyl azides (8) in ethanethiol in the presence of sulfuric acid gave only reduction products, 3-aminoquinolines. On the other hand, irradiation of the azides (8a,b) in ethanethiol in the absence of the acid afforded 3-amino-4-ethylthioquinolines (9a: 35%; 9b: 72%);[6] 3-aminoquinoline (10) was also formed in the reaction of 8a. Thermolysis of 8a and 8b by refluxing in ethanethiol gave the same ethylthio compounds, 9a (86%) and 9b (90%), as the sole products.



Scheme 2

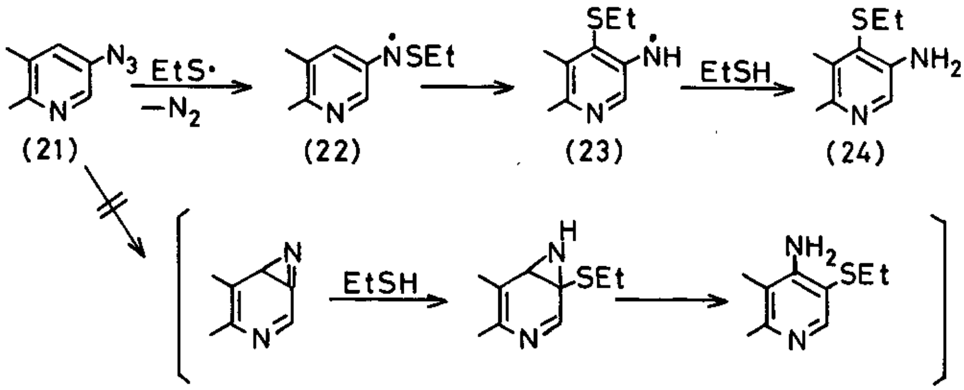
4-Isoquinolyl azide (11a), upon either irradiation or heating in ethanethiol alone, gave two kinds of ethylthio compounds (12: $h\nu$ 41%; heat 32% and 13a: $h\nu$ 10%; heat 21%) accompanied with 4-aminoisoquinoline (14: $h\nu$ 40%; heat 32%). In contrast, 4-azidoisoquinoline N-oxide (11b) gave only 4-amino-1-ethylthioisoquinoline N-oxide (13b) by either photolysis (65%) or thermolysis (87%). However, 4-quinolyl azide (15a) and its N-oxide (15b) did not give any ethylthio compounds but gave the reduction products (16) in 70-90% yields.

As an example of benzopyridine azides having an azido group in the benzene ring, 8-quinolyl azide (17) was choiced. Its reaction under similar conditions resulted in the formation of 7-ethylthio- (18: $h\nu$ 34%; heat 60%) and 5-ethylthio-8-aminoquinoline (19: $h\nu$ 11%; heat 4%) together with 8-aminoquinoline (20: $h\nu$ 36%; heat 30%) (Scheme 2).[7]

The Structures of the new ethylthio compounds were confirmed by NMR spectral analysis of their deamination products prepared through the diazonium salts and also the desulfurization products obtained by treatment with Raney nickel.

The positions of the amino and the ethylthio groups in the products (9, 12, 13, 18, and 19) indicate that the present reactions do not involve azirine intermediates. Although the results are somewhat similar to those obtained from the reactions under acidic conditions,[3,4] it is unlikely that these reactions follow the course involving nitrenium intermediates taking account of the reaction conditions.

It seems rather reasonable to assume that these reactions proceed by a radical mechanism shown in Scheme 3. Decomposition of the azides (21) might be induced by thiyl radicals to give the radical intermediates (22), which may be converted



Scheme 3

to the products (**24**) through the second radicals (**23**), as suggested by Shingaki for the decomposition of phenyl azides in thiols.[8] In the case of the 4-quinolyl azide (**15b**), the electron-donating effect of the conjugated N-oxide group may accelerate decomposition to nitrene. On the contrary, the electron-withdrawing effect of the conjugated ring nitrogen in **15a** may inhibit the decomposition catalyzed by thiyl radicals. Thus, the nitrene formation is preferable to the radical formation in these cases and the reduction of nitrenes by ethanethiol readily occurs to give the products (**16**).[9]

Studies on the detailed mechanism of the reactions and on applications of these results to other systems are in progress.

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3. H. Sawanishi, T. Hirai, and T. Tsuchiya, *Heterocycles*, 1982, **19**, 1043.
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5. Photolyses were carried out under a nitrogen atmosphere in an immersion apparatus equipped with a halogen lamp, which was cooled internally with running water.
6. Satisfactory elemental analyses and spectral data were obtained for all new compounds reported.
7. It has been reported that the similar photolytic decomposition of 8-quinolyl azide (**17**) in ethanethiol gave 7-amino-8-ethylthioquinoline *via* the azirine intermediate; this result is different from that of the present report. [S.E. Carroll, B. Nay, E.F.V. Scriven, H. Suschitzky, and D.R. Thomas, *Tetrahedron Lett.*, 1977, 3175; Z.U. Khan, B. Nay, E.F.V. Scriven, and H. Suschitzky, *J. Chem. Soc., Perkin Trans. I*, 1982, 671.]
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