

REACTIONS OF PYRIDYL, QUINOLYL, AND ISOQUINOLYL AZIDES:
INTRODUCTION OF HALOGENO, ALKOXY, AND ALKYLTHIO GROUPS

Hiroyuki Sawanishi, Toyoko Hirai, and Takashi Tsuchiya
School of Pharmacy, Hokuriku University,
Kanagawa-machi, Kanazawa 920-11, Japan

Azides have been widely used as reactive intermediates in organic syntheses and it is known that the photolysis of azidoquinolines in the presence of bases such as amines gives ortho-substituted amino derivatives via azirine or azacycloheptatetraene intermediates as shown in Scheme 1 (Type-A), whereas the azides give dimerization products by irradiation in neutral conditions. In connection with the above results and those of phenyl azides, we examined the photochemical and thermal behaviors of the title azides in various conditions.

(i) Photolysis of the title azides in hydrohalogenoic acids gave the α -halogeno amino compounds via the nitrenium ion intermediates as shown in Scheme 2 (Type-B). Heating of the azides in hydrohalogenoic acids also gave the same products, but the thermolysis requires more drastic conditions and gives lower yields of the products than those for the photolysis.

(ii) Photolysis of the azides in alcohols containing sulfuric acid gave either type-A or type-B α -alkoxy amino derivatives, whose formation depends on the position of the azido group, whereas their thermolysis in the same solvents gave no such products.

(iii) Both photolysis and thermolysis of the azides in alkanethiol gave the α -alkylthio amino compounds, type-B products, via the radical process as shown in Scheme 3 (Type-C).

