

PHOTOCHEMISTRY OF o-NITROBENZALDEHYDE N-ACYLHYDRAZONES

FORMATION OF 1-ALKYL-5-NITROPHthalAZINES AND BENZOTRIAZINONE, AND GENERATION OF  
BENZYNE VIA AN INTERMEDIACY OF INDAZOLONE

Yoshifumi Maki, Takashi Furuta, Masayuki Kuzuya, and Mikio Suzuki  
Gifu College of Pharmacy, Mitahora, Gifu 502

Photochemistry of o-nitrobenzaldehyde N-acylhydrazones was investigated. The most intriguing conclusion is that the nature of substituents on the hydrazone moiety markedly influences on the photochemical behavior of these compounds.

Irradiation of o-nitrobenzaldehyde N-alkyl-N-acetylhydrazones in methanol gave ultimately benzyne and alkyl acetamide. It was proved that the photoreaction proceeds via decomposition of o-(N-acetyl-N-alkyltriazeno)benzoic acids derived from 1-hydroxy-2-(N-alkylacetamido)-3(2H)-indazolones which are cyclic forms of o-nitrosobenzoyl-N-acetyl-N-alkylhydrazides initially produced in an analogous fashion to the o-nitrosobenzylideneaniline rearrangement. o-(N-Acetyl-N-alkyltriazeno)benzoic acids, which can be utilized thermally and photochemically as a benzyne precursor, were obtained by irradiation of o-nitrobenzaldehyde N-alkyl-N-acetylhydrazone in benzene followed by alkaline hydrolysis in excellent yields.

In the case of o-nitrobenzaldehyde N-acetyl-N-acylhydrazones, analogous irradiation resulted in the formation of 1-substituted-5-nitrophthalazines and 1,2,3-benzo-4(3H)-triazinone. Irradiation of o-nitrobenzaldehyde N-acylhydrazones gave 1-substituted-5-nitrophthalazines in preparative yields, accompanied with benzyne generation only as a minor process.

The formation of 1-substituted-5-nitrophthalazines can be explained in terms of the photoelectrocyclic reaction of the six-electron system and subsequent elimination of acetic acid or water. This type of photocyclization can be applied to the synthesis of various 1-substituted-5-nitrophthalazines. On the other hand, the formation of 1,2,3-benzo-4(3H)-triazinone appears to involve the rearrangement of o-nitrosobenzoyl-N-acetyl-N-acylhydrazide which cyclizes in a fashion different from benzyne generation.