Photochemistry of *o*-Nitrobenzaldehyde *N*-Acetyl-*N*-alkylhydrazones Resulting in the Formation of Benzyne

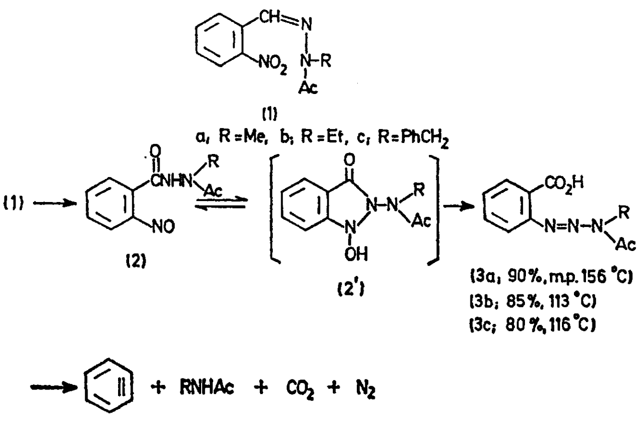
By Y. Maki,* T. Furuta, M. Kuzuya, and M. Suzuki
(*Gifu College of Pharmacy, Mitahora, Gifu, Japan*)

Summary Photolysis of *o*-nitrobenzaldehyde *N*-acetyl-*N*-alkylhydrazones gave benzyne *via* *o*-nitrosobenzoyl-*N*-acetyl-*N*-alkylhydrazides and *o*-(*N*-alkyl-*N*-acetyltriazeno)benzoic acids.

A number of photo-induced intramolecular rearrangements of nitroaromatics are well known in which the nitro group is reduced to a nitroso function while an oxygen atom is apparently transferred to an *ortho*-substituent.[1] The photoconversion of *o*-nitrobenzylideneaniline into *o*-nitrosobenzanilide[2,3] involves such a typical intramolecular oxidation–reduction process.

We found that irradiation of *o*-nitrobenzaldehyde *N*-acetyl-*N*-alkylhydrazones (**1**) results in the generation of benzyne *via* decomposition of *o*-(*N*-acetyl-*N*-alkyltriazeno)benzoic acids (**3**) derived from *o*-nitrosobenzoyl-*N*-acetyl-*N*-alkylhydrazides (**2**) which are initially formed in an analogous fashion to the *o*-nitrobenzylideneaniline rearrangement. This type of photochemistry is unusual and provides a new method for producing benzyne.

Although no significant change was observed in the photolysis of *o*-nitrobenzaldehyde methylhydrazone, its *N*-acetyl derivative (**1a**) in methanol reacted readily when irradiated using a high-pressure mercury lamp under nitrogen through Pyrex. The photoreaction of (**1a**) was monitored by n.m.r. spectroscopy using CD_3OD as solvent.



Scheme

The spectral changes indicated that the photolysis proceeds cleanly *via* a detectable intermediate.

G.l.c.–mass spectral analysis of the reaction mixture indicated the presence of *N*-methylacetamide, and a compound (M^+ *m/e* 228) believed to be triphenylene.† Irradiation of a mixture of (**1a**) and tetracyclone in methanol gave 1,2,3,4-tetraphenylnaphthalene in *ca.* 10% yield. These experiments clearly indicate that photolysis of (**1a**) generates benzyne ultimately.

When (**1a**) in benzene was irradiated, the reaction mixture deposited (**2a**),‡ m.p. 150 °C, as colourless crystals (*ca.* 90%). The n.m.r. spectrum of (**2a**) in CD_3OD was consistent with that of the intermediate detected during photolysis of (**1a**). In the dark, (**2a**) in methanol was gradually converted into *o*-(*N*-acetyl-*N*-methyltriazeno)-benzoic acid (**3a**), presumably *via* the cyclic form (**2′**) of (**2a**). This conversion was accelerated to some extent by irradiation. Photolysis of (**3a**) in methanol in the presence of tetracyclone caused rapid decomposition leading to *N*-methylacetamide (85%), 1,2,3,4-tetraphenylnaphthalene (15%), and undetermined products. These photochemical reactions take place by the route shown in the Scheme. Similar reactions were observed in the cases of *N*-ethyl and *N*-benzyl derivatives (**1b, c**).

Mild alkaline treatment of (**2**) (3% NaOH at room temp.), followed by acidification (5% HCl), gave (**3**) quantitatively. Shimamura *et al.*[4] have reported that thermolysis of *o*-dimethyltriazenobenzoic acid produces benzyne. Thermolysis of (**3**) also gave benzyne, which was trapped by tetracyclone.

A combination of photolysis of (**1**) in benzene and subsequent alkaline hydrolysis of the isolated (**2**) provides a new method for the preparation of (**3**), which can be used as a benzyne precursor.

(*Received*, 28*th May* 1975; *Com.* 586.)

---

† It was reported that photolysis of phthaloyl peroxide or benzocyclobutene produces benzyne which leads to the formation of triphenylene and other polymeric compounds (*cf.* O. L. Chapman, K. Matles, C. L. McIntoshi, J. Pakanski, G. V. Colden, and G. Orr, *J. Amer. Chem. Soc.*, 1973, **95**, 6134.

‡ All new compounds gave satisfactory microanalytical results and spectral data consistent with their structures. The compound (**2a**) appears to exist in the dimeric form rather than the cyclic form (**2a′**), in the solid state. The i.r. spectrum (KBr) exhibited bands which were assigned as follows: 3230 (νNH), 1680 (νC=O), 1530 and 1340 cm^{-1} (δNH). The NH deformation bands were confirmed by a deuterium-labelling experiment. The colourless appearance and mass spectral data (M^+ *m/e* 442) of the compound also supports this formulation.

[1] For a review, see H. A. Harison, 'The Chemistry of the Nitro and Nitroso groups. Part I,' Wiley-Interscience, NewYork, 1969, p. 165; Y. Maki, M. Suzuki, T. Hosokami, and T. Furuta, *J.C.S. Perkin I*, 1974, 1354, and references therein.
[2] F. Sachs and R. Kempf, *Ber.*, 1902, **35**, 2704.
[3] H. Hadjoudis and E. Hayon, *J. Phys. Chem.*, 1970, **74**, 2224, 3184.
[4] J. Nakayama, M. Yoshida, and O. Shimamura, *Chem. Letters*, 1973, 451.