J.C.S. CHEM. COMM., 1975

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-Nalkylhydrazones gave benzyne via o-nitrosobenzoyl-Nacetyl-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 Nacetyl-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-Nalkylhydrazides (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 CD₈OD as solvent.



J.C.S. CHEM. COMM., 1975

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), tm.p. 150 °C, as colourless crystals (ca. 90%). The n.m.r. spectrum of (2a) in CD₃OD 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 odimethyltriazenobenzoic 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, 28th 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 (ν NH), 1680 (ν C=O), 1530 and 1340 cm⁻¹ (δ NH). 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 H. Hadjoudis and E. Hayon, J. Phys. Chem., Chem. Chem. 2012, 451.

⁴ J. Nakayama, M. Yoshida, and O. Shimamura, Chem. Letters, 1973, 451.