

PHOTOCHEMICAL REACTIONS OF 2-BENZYLIDENEHYDRAZINOPYRIMIDINES

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Under a nitrogen atmosphere, anti-isomers of 2-benzylidenehydrazinopyrimidines easily underwent isomerization to their syn-isomers by irradiation with an ultraviolet light over a benzene solution, but in the presence of oxygen, photosensitized auto-oxidation occurred to afford 3-aryl-1,2,4-triazolo[4,3-a]pyrimidines. When irradiated in the same manner, 2-benzylidenehydrazino-1,3,5-triazine derivative decomposed into benzaldehyde and 2-hydroxy-1,3,5-triazine.

This communication describes some information on the photochemical reactivities of 2-benzylidenehydrazinopyrimidine derivatives observed during the course of the light-stability tests.

Isomerization of 2-(2,6-dichlorobenzylidenehydrazino)pyrimidine from the E-isomer(1a) to the Z-isomer(1b) has already been reported by us in detail.¹ In the present study we found that an analogous compound, 2-(2,6-dichlorobenzylidenehydrazino)-4,6-dimethylpyrimidine was also isomerized from the E-isomer(2a) to the Z-isomer(2b) by

irradiation with a high-pressure mercury lamp under a nitrogen atmosphere.

For elucidation of the structures of 2a and 2b, NOE was used in a similar manner as in the case of 1a and 1b. When irradiated on the NH proton, no NOE for CH proton of 2b was observed, but a 31.8 % NOE was detected for the CH proton of 2a. Moreover, a 20.2 % NOE enhancement to the NH proton on irradiation of the CH proton in 2a was recognized. The above results indicate that in the molecule of 2a the azomethine proton must be located close to the NH proton, suggesting the syn-position to one another; while in the molecule of 2b the CH and NH protons are not located on the same side of the C:N bond, implying the anti-position. Consequently, the structures of these isomers were assigned E to 2a and Z to 2b as shown in Chart 1.

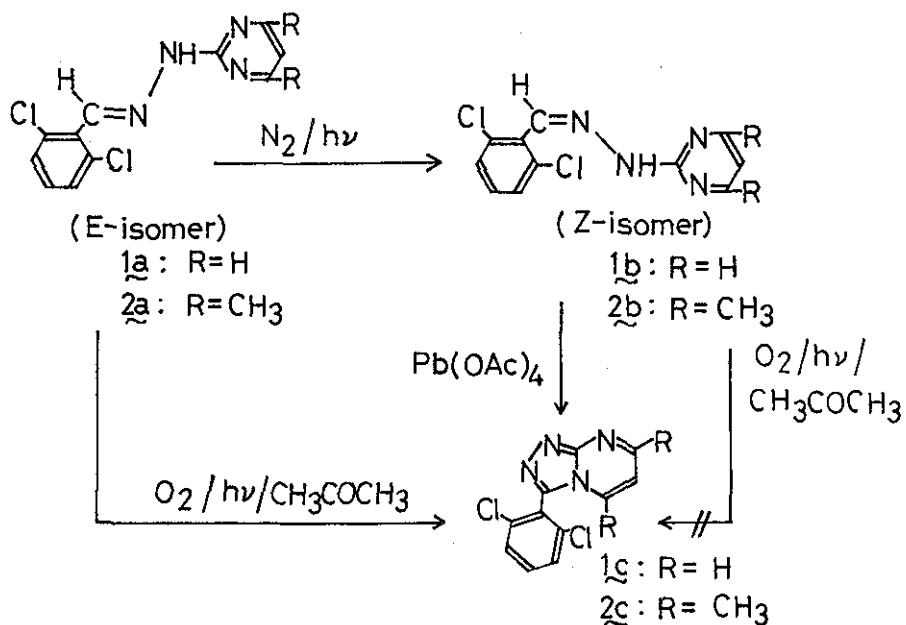


Chart 1

On the other hand, when a solution of 2a was exposed to the sunlight or irradiated with a high-pressure mercury lamp for a long time in the presence of air, a trace of an unknown fluorescent compound was detected by thin-layer chromatography (TLC). The irradiation along with air-bubbling resulted in 0.5-1.2% formation² of the above unknown compound, and the addition of a small amount of benzophenone increased the yield of the unknown compound to 15 %.² Finally, the above compound was obtained in 37 % yield² when acetone was used as a photosensitizer instead of benzophenone. This photochemical reaction was scarcely affected by addition of methylene blue or Rose Bengal, and no solvent effect by methanol or benzene was observed. Use of acetone as solvent and photosensitizer was most effective for formation of the unknown compound. Under the same conditions, 2b did not afford any fluorescent compound.

The fluorescent substance was isolated by column chromatography on silica gel, and crystallized from aqueous methanol to obtain colorless needles, $C_{13}H_{10}N_4Cl_2$, which melt at 247-249°. By comparison of elemental analysis, TLC, and infrared (IR) and nuclear magnetic resonance (NMR) spectra, this compound was established to be 3-(2,6-dichlorophenyl)-5,7-dimethyl-1,2,4-triazolo[4,3-a]pyrimidine (2c) prepared by the reaction of 2a with lead tetraacetate according to Bower's procedure.³ 3-(2,6-Dichlorophenyl)-1,2,4-triazolo[4,3-a]pyrimidine (1c) (mp 204-205°, 22.5 %) was obtained from 1a by the similar procedure.

Next, when 2-(3,4-dimethoxybenzylidenehydrazino)-4,6-dipiperidino-1,3,5-triazine (3a) (E-isomer), an analogue of 2-benzylidenehydrazinopyrimidines, was irradiated in acetone-methanol (3:1) with a high-pressure mercury lamp with air-bubbling for 12 hr, the products

isolated were not 1,2,4-triazolo[4,3-a][1,3,5]triazine derivative (3c), but veratraldehyde (93.3 %) and 2-hydroxy-4,6-dipiperidino-1,3,5-triazine (7) (mp 269-271° (decomp.), 54.2 %). On the other hand, when 3a was irradiated under a nitrogen atmosphere, only a half of the material was isomerized to the Z-isomer (3b), which was hardly purified by the ordinary silica gel column chromatography because 3b was quite labile reconverting readily to 3a.

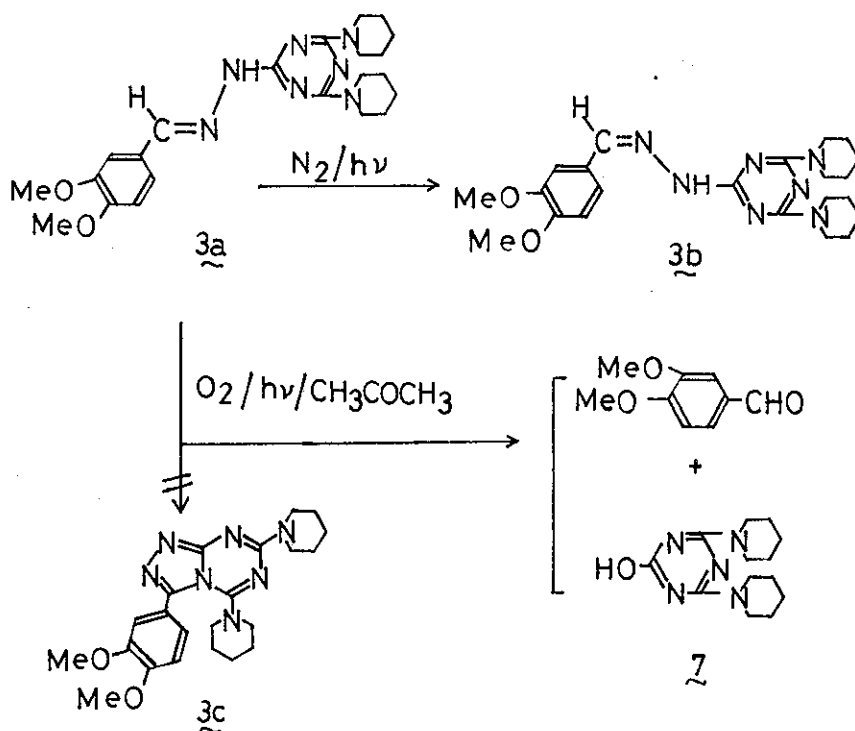


Chart 2

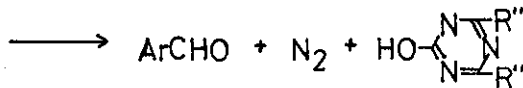
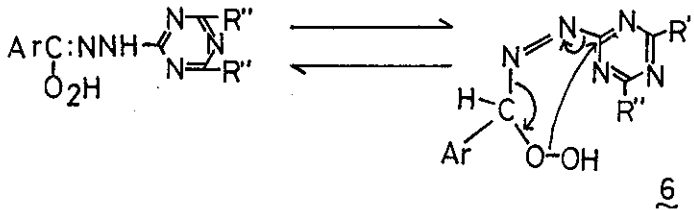
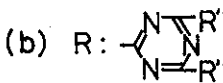
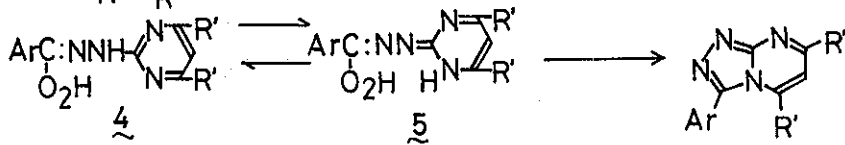
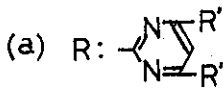
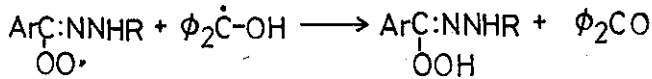
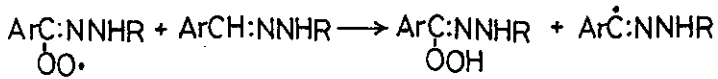
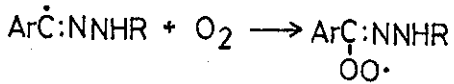
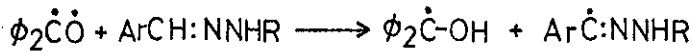
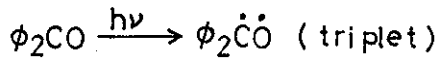


Chart 3

On the basis of these findings in the photochemical reactions of 1a and 2a, it is likely that the photochemical reactions described above are grouped as the type I photo-oxygenation according to Gollnick's classification.⁴ Namely, its main feature is abstraction of hydrogen by the sensitizer (in its excited triplet state) followed by addition of oxygen to the newly created radical. The mechanisms of the present reactions may be summarized as shown in Chart 3.

It has already been pointed out that the products in the photochemical reaction of 1,3,5-triazine differ from those in the case of pyrimidines. This can be depicted by two different routes, (a) and (b), in Chart 3. In the case of 3a, the contribution of a 5-type tautomer might be prohibited due to the highly symmetric nature of the triazine ring with the three nitrogen substituents on the 2-, 4-, and 6-positions. Consequently, formation of 1,2,4-triazolo[4,3-a]-[1,3,5]triazine(3c) via process (a) would not occur.

The unsuccessful photo-oxidation of 2b to 2c may be accounted for by the difficulty in H₂O₂-elimination because of the fixation of hydroperoxy group and pyrimidine ring in the anti-position in connection with the C:N bond in the 5 derived from 2b.

The starting material, 1a, was prepared by the method described in literature.⁵ While 2a and 3a were obtained from the corresponding benzaldehydes and 2-hydrazino derivatives according to the procedure of Sirakawa.⁶ The photochemical reactions were run on 1.5-3.0 g of sample in solution(300 ml) using a UM-103 reactor(Ushio Electric Co. Ltd.) under bubbling with gas(nitrogen or air) passed through the inlet tube from compressed gas source.

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