[Chem. Pharm. Bull. 22(6)1269—1274(1974)]

UDC 547.791'546.21.057

Photochemical Synthesis of Condensed Triazole N-Oxide[1]

Yoshifumi Maki, Mikio Suzuki, Keiji Izuta, and Shunji Iwai

Gifu College of Pharmacy[2]

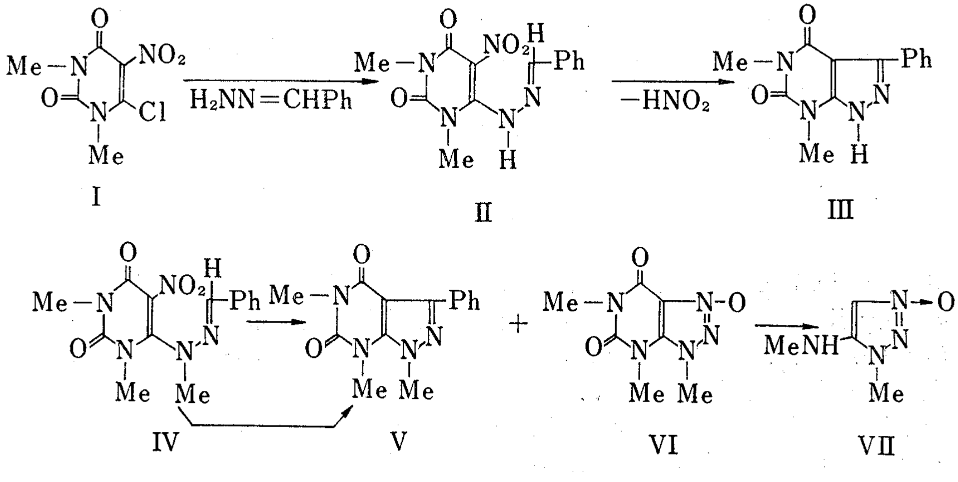
(Received September 7, 1973)

Photolysis of 1,3-dimethyl-5-nitro-6-benzylidenemethylhydrazinouracil (IV) resulted in the formation of 1,5,7-trimethyl-3-phenyl-4,6(5H,7H)-pyrazolo(3,4-*d*)pyrimidinedione (V) and 3,4,6-trimethyl-5,7(4H,6H)-triazolo(4,5-*d*)pyrimidinedione 1-oxide (VI). Upon irradiation of 1,3-dimethyl-5-nitro-6-acetophenylidenemethylhydrazinouracil (VIII), however, VI was obtained exclusively in excellent yield. On the basis of mechanistic consideration on these photocyclizations, a new photochemical synthesis of condensed 3-alkyltriazole 1-oxides was developed.

A recent article[3] from our laboratory has described a convenient and widely applicable synthetic route to pyrazolo(3,4-*d*)pyrimidines by the thermal reaction of 1,3-dimethyl-5-nitro-6-chlorouracil (I) with hydrazones of a wide variety of aldehydes and ketones. This reaction apparently involves a thermal cyclization of the initially formed 1,3-dimethyl-5-nitro-6-benzylidene (or alkylidene) hydrazinouracil. A representative example is illustrated in Chart 1 (I→II→III).

In contrast with 1,3-dimethyl-5-nitro-6-benzylidenehydrazinouracil (II), the thermal cyclization of its N-methyl derivative (IV) leading to 1,5,7-trimethyl-3-phenyl-4,6(5H, 7H)-pyrazolo(3,4-*d*)pyrimidinedione (V) has been achieved only in a poor yield.[3]

In a continuation of the study of this system, we observed that IV underwent photocyclizations to afford V and 3,4,6-trimethyl-5,7(4H, 6H)-triazolo(4,5-*d*)pyrimidinedione 1-oxide (VI). Exclusive formation of VI was attained by virtue of irradiation of 1,3-dimethyl-5-nitro-6-acetophenylidenemethylhydrazinouracil (VIII) instead of IV.



Ph=phenyl

Chart 1

---

[1] A part of this work has presented in a preliminary form. Y. Maki, K. Izuta, and M. Suzuki, *Tetrahedron Letters*, **1972**, 1973.

[2] Location: *36–492, Mitahora, Gifu.*

[3] Y. Maki, K. Izuta, and M. Suzuki, *Chem. Commun.*, **1971**, 1442.

These results provide new examples of photocyclizations which involve novel, nonoxidative photocyclization with elimination of a nitro group, and photochemical interaction between a nitro group and a hydrazone C=N bond.

The present paper describes these remarkable observations and their extension to a new photochemical synthesis of condensed triazole N-oxides which may be widely applicable.

A solution of IV in degassed benzene was irradiated under nitrogen with a 100 W high-pressure mercury arc lamp surrounded by a water-cooled Pyrex filter for 10 hr. After being allowed to stand, the reaction mixture deposited a product, mp 293°, in 35% yield. The mother liquor was concentrated to isolate another product, mp 188°, in 40% yield.

The latter compound was identical in every respect with V obtained by the thermal cyclization of IV as previously reported.[3]

The mass spectrum of the former compound revealed a strong M-16 peak indicating the presence of a labile oxygen, most probably an N-oxide grouping. This conclusion was confirmed by its deoxygenation to the known 3,4,6-trimethyl-5,7(4H, 6H)-triazolo(4,5-*d*)pyrimidinedione.[4] Thus, the former product must be one of the two possible 1- and 2-oxides.

Mild alkaline treatment of the former compound led to the formation of 3-methyl-4-methylaminotriazole 1-oxide (VII) in high yield accompanied with decarboxylation. The facile decarboxylation is explicable in terms of placement of the N-oxide grouping on the ring nitrogen (N_1) adjascent to the carboxyl grouping in the initially formed carboxylic acid. As a consequence, the former compound can be assigned to the 1-oxide structure (VI). This conclusion was also deduced from an unequivocal synthesis of 3-methyl-6-chlorobenzotriazole 1-oxide (X) obtained by irradiation of 2-benzylidenemethylhydrazino-5-chloronitrobenzene (IX) as described later.

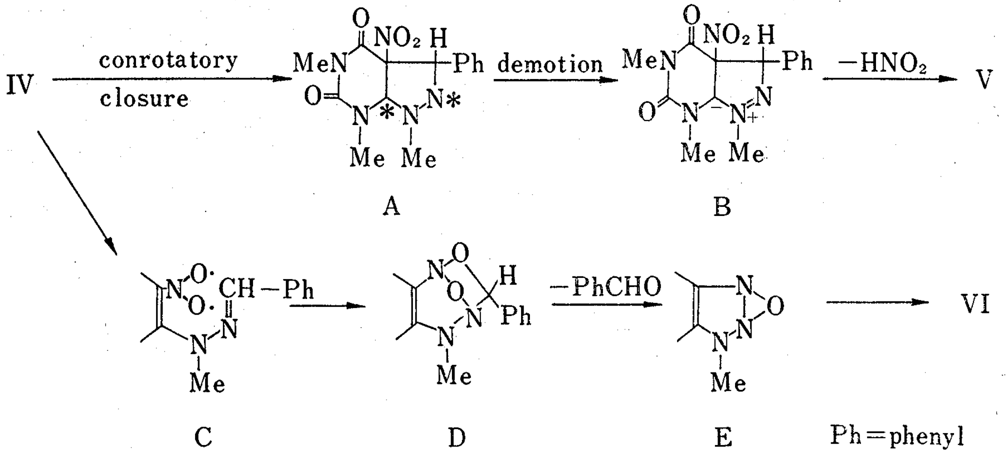


Chart 2

The photochemical cyclization of IV to V seems to be best explained in terms of a photochemical electrocyclic reaction as previously predicted in the photocyclization of the arylated enamines[5] (see Chart 2). Subsequent collapsed of the intermediate (B) thus formed with the loss of nitrous acid could lead to V.

The formation of VI appears to be initiated by photocycloaddition of an excited nitro group (C) to the hydrazone C=N bond to form a cyclic intermediate (D) (or its equivalent biradical intermediate). An analogous addition of the nitro group to the C=N bond of a

---

4) The deoxygenated triazolopyrimidine (W. Pfleiderer and G. Nubel, *Chem. Ber.*, **98**, 1060 (1965)) was hydrolyzed to 1-methyl-5-methylaminotriazole-4-carboxylic acid, mp 143°, upon treatment with alkali under the same conditions. Smooth decarboxylation of the *ortho*-situated carboxyl grouping to the N-oxide grouping has been observed in pyrazine and pyridine systems (*cf.* E.C. Taylor, Y. Maki, and A. Mckillop, *J. Org. Chem.*, 37, 1602 (1972) and references cited).

5) O.L. Chapman, G.L. Eian, A. Bloom, and J. Clardy, *J. Am. Chem. Soc.*, **93**, 2918 (1971).

Schiff base has been proposed previously[6] and recently it has been shown that the photochemical addition of aromatic nitro compounds to alkene gives 1,3,2-dioxazolidine.[7] The loss of benzaldehyde from the intermediate (D) could lead to an oxadiaziridine intermediate (E) (or its equivalent biradical intermediate), which affords VI. Posturation of an oxadiaziridine intermediate has precedent in the photochemical isomerization of azoxy compounds.[8] The exclusive formation of 1-oxide without 2-oxide, however, may favor to chose biradical intermediates over cyclic intermediates.

On the basis of mechanistic consideration of the above photocyclizations, if VIII is employed as a starting material instead of IV, the photocyclization could occur to give VI exclusively because of no possibility of the nitrous acid elimination in a cyclic intermediate (Me in place of H in (B)) which appears to be reversible to VIII.[9]

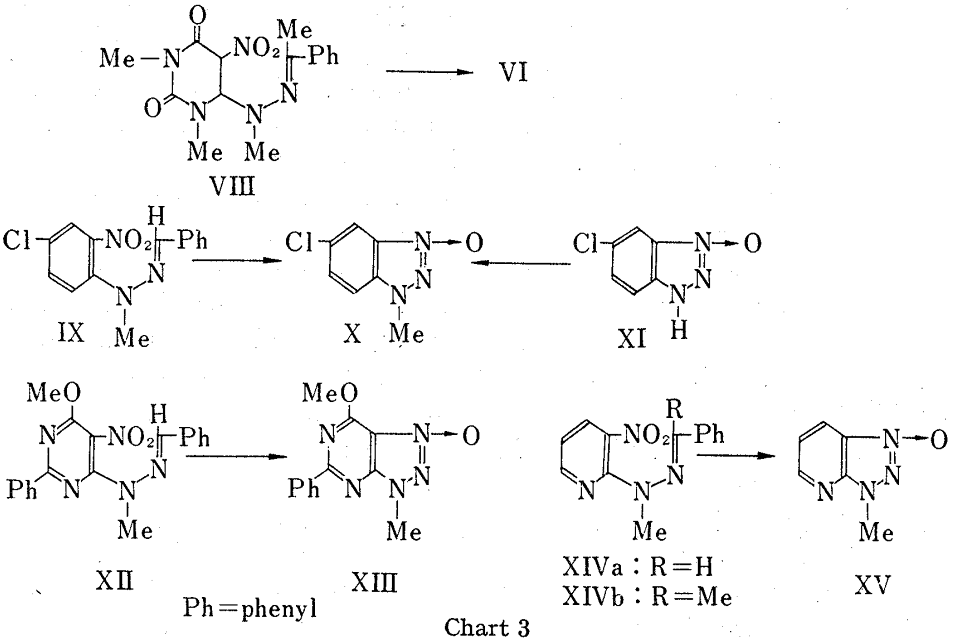


Chart 3

TABLE I. The Apparent Effect of Various Wave-length Lights on the Photochemical Formation of 3,4,6-Trimethyl-5,7(4H,6H)-triazolo(4,5-*d*)pyrimidinedione 1-Oxide (VI)[a] (in MeCN)

Wave-length of light (mμ)	Relative intensity[b] at 236 mμ
391	1.0
364	1.9
338	2.5
311	1.8
285	0.04

a) A solution of 1,3-dimethyl-5-nitro-6-acetophenylidenemethylhydrazinouracil (VIII) in MeCN was irradiated with a Concave Radiating Monochrometer (JASCO-Model CRM-FA).

b) UV spectra of the reaction mixture after irradiation for 30 min were measured. Absorbances of the characteristic absorption band (236 mμ) of VI for each reaction mixture were corrected on the basis of the energy distribution curve of the light source employed. The relative intensities were obtained by setting the UV absorbance of the reaction mixture irradiated with 391 mμ light as a standard.

---

[6] E.C. Taylor, B. Furth, and M. Pfau, *J. Am. Chem. Soc.*, **47**, 1400 (1965).

[7] J.L. Charlton, C.L. Liao, and P. de Mayo, *J. Am. Chem. Soc.*, **93**, 2463 (1971).

[8] K.G. Taylor and T. Riehl, *J. Am. Chem. Soc.*, **94**, 250 (1970); *idem, ibid.*, **93**, 7337 (1971).

[9] Attempts to obtain exclusively either V or VI upon irradiation of IV by variation of solvents and addition of sensitizers were unsuccessful.

In this concept, VIII was irradiated in degassed acetonitrile for 10 hr. As was expected, a clean reaction occurred and VI was obtained in 90% yield. This photocyclization also proceeded in benzene, methanol–acetonitrile (1: 1) and acetone in 58%, 79% and 90% yields respectively.

The apparent effect of wave-length of a light source on the photocyclization was examined by using a monochrometer. Table I shows that a light at 338 mμ is most efficient for the present photoconversion.

When 2-benzylidenemethylhydrazino-5-chloronitrobenzene (IX) in benzene (or acetonitrile) were irradiated for 20 hr, 3-methyl-6-chlorobenzotriazole 1-oxide (X) and its deoxygenated product were isolated in 10% and 17% yields respectively.

The synthesis of X was accomplished as follows: 2,5-dichloronitrobenzene was heated in excess hydrazine hydrate and the resulting hydrazine salt of 6-chlorobenzotriazole 1-oxide (XI) was treated with hydrochloric acid to liberate XI in 60% yield. N-Methylation of XI was achieved unambiguously according to procedure[10] previously reported in the N-methylation of benzotriazole 1-oxide (reflux in dimethyl sulfate). The N-oxide (X) thus prepared was identical in every respect with a sample obtained by irradiation of IX.

It is worthwhile noting that IX did not cyclize to the corresponding 1-methylbenzopyrazole in a sharp contrast to the case of IV. This marked difference can be ascribed in part to the facility of a 5-nitro group on the uracil ring of IV to act as a good leaving group.

Similar observations were made in the photocyclization of 2-phenyl-4-methoxy-5-nitro-6-benzylidenemethylhydrazinopyrimidine (XII) and 3-nitro-2-benzylidenemethylhydrazinopyridine (XIVa). Irradiation of XII and XIVa under the conditions similar to the previous cases resulted in the exclusive formation of 3-methyl-5-phenyl-7-methoxytriazolo(4,5-*d*)-pyrimidine 1-oxide (XIII) and 3-methyltriazolo(4,5-*b*)pyridine 1-oxide (XV) in 50% and 35% yields respectively. An improved yield of XV (65%) was obtained by irradiation of acetophenylidene derivative (XIVb).

In view of the ready availability of the requisite nitro compounds having an *ortho*-situated alkylhydrazone moiety, this type of photochemical reaction is flexible and has considerable generality. In particular, this is advantageous for the synthesis of condensed 3-alkyltriazole-1-oxides,[11] which is encounted by difficulty under the usual thermal reaction.[12]

Experimental[13]

General Irradiation Procedure——Irradiations were conducted in an immersion reactor (Rikosha Model UVL-300P) using 100 W high-pressure mercury arc lamp with a water-cooled Pyrex filter. Prior to irradiation, the solution was flushed with nitrogen and was bubbled through the solution constantly during irradiation.

Photolysis of 1,3-Dimethyl-5-nitro-6-benzylidenemethylhydrazinouracil (IV)——A solution of IV[3] (0.8 g) in benzene (200 ml) was irradiated for 10 hr. After being allowed to stand at room temperature for several hr, the reaction mixture deposited 3,4,6-trimethyl-5,7(4H,6H)-triazolo(4,5-*d*)pyrimidinedione 1-oxide (VI), mp 293°, which was recrystallized from acetone, in 35% yield. NMR (CF_3COOH) τ: 6.44 (3H, s, –NC$\underline{H}_3$), 6.01 (3H, s, –N–C$\underline{H}_3$), 5.61 (3H, s, –NC$\underline{H}_3$). UV λ_{max}^{MeCN} mμ (log *e*): 236 (4.59), 270 (4.37). Mass Spectrum *m/e*: 195 (M^+–16). *Anal.* Calcd. for $C_7H_9O_3N_5$: C, 39.81; H, 4.30; N, 33.17. Found: C, 38.89; H, 4.48; N, 33.84. The mother liquor was concentrated and the solid residue was recrystallized from EtOH

---

10) O.S. Blady and J.N.E. Day, *J. Chem. Soc.*, **1928**, 193.

11) The procedure is not adequate for the synthesis of N-nonsubstituted triazole N-oxides, *e.g.*, 1,3-dimethyl-5-nitro-6-acetophenylidenehydrazinouracil (H in place of Me in the N_1-position of VIII) gave photochemically the corresponding pyrazolo(3,4-*d*)pyrimidine in 10% yield together with undetermined byproducts.

12) For a review, see D.N. Preston and G. Tennant, *Chem. Rev.*, **72**, 646 (1972). For example, attempts to prepare VI under the thermal conditions were unsuccessful.

13) All melting points are uncorrected. Infrared (IR) spectra were run on a Hitachi-215 spectrometer. Nuclear magnetic resonance (NMR) spectra were recorded at 60 MHz with a Hitachi R-20B using TMS as an internal standard. The following abbreviations are used: s=singlet, d=doublet, t=triplet.

to give 1,5,7-trimethyl-3-phenyl-4,6(5H,7H)-pyrazolo(3,4-*d*)pyrimidinedione (V), mp 188°, in 40% yield. V was identical in every respect with a sample obtained by the thermal cyclization of IV[3].

Photolysis of 1,3-Dimethyl-5-nitro-6-acetophenylidenemethylhydrazinouracil (VIII)——To a solution of I (2.2 g) in $CHCl_3$ (66 ml) was added acetophenylidenemethylhydrazone (4.4 g) in EtOH (10 ml) in small portions with stirring over a period of 1 hr. The reaction mixture was evaporated to dryness under reduced pressure and the oily residue was triturated with a small amount of ether–MeOH to give a solid mass. The powdery mass thus obtained was recrystallized from acetone–EtOH to give VIII (3.0 g), mp 203°, as yellow prisms. NMR (DMSO-d_6):τ 7.67 (3H, s, C–$C\underline{H}_3$), 6.77 (3H, s, N–$C\underline{H}_3$), 6.73 (3H, s, N–$C\underline{H}_3$), 2.71—2.61 (5H, m, aromatic protons). UV $\lambda_{\max}^{\mathrm{MeCN}}$ mμ (log *e*): 272(4.24), 320(3.95). *Anal.* Calcd. for $C_{15}H_{17}O_4N_5$: C, 54.37; H, 5.17; N, 21.14. Found: C, 54.43; H, 5.32; N, 21.34.

A solution of VIII (1.0 g) in MeCN (200 ml) was irradiated for 10 hr. The irradiated solution was allowed to stand at room temperature to deposit a colorless crystalline solid (0.31 g). After removal of the solid by filtration, the filtrate was evaporated under reduced pressure and the residue was washed with EtOH to give an another crop of the colorless solid (0.27 g). The combined solid was recrystallized from acetone to give 3,4,6-trimethyl-5,7(4H,6H)-triazolo(4,5-*d*)pyrimidinedione 1-oxide (VI) (0.55 g), mp 292—294°, as colorless prisms. Mass Spectrum *m/e*: 195 (M^+–16). NMR (CF_3COOH) τ: 6.44 (3H, s, N-$C\underline{H}_3$), 6.01 (3H, s, N–$C\underline{H}_3$), 5.61 (3H, s, N–$C\underline{H}_3$). UV $\lambda_{\max}^{\mathrm{MeCN}}$ mμ (log *e*): 236(4.59), 270(4.37). *Anal.* Calcd. for $C_7H_9O_3N_5$: C, 39.81; H, 4.30; N, 33.17. Found: C, 39.89; H, 4.48; N, 33.84.

Hydrolysis of 3,4,6-Trimethyl-5,7(4H,6H)-triazolo(4,5-*d*)pyrimidinedione 1-Oxide (VI)——A suspension of VI (0.26 g) in 25% KOH (5 ml) was heated under reflux for 1 hr. After cooling, the reaction mixture was neutralized with dil. HCl and concentrated under reduced pressure to dryness. The residue was recrystallized from acetone to give 3-methyl-4-methylaminotriazole 1-oxide (VII) (0.15 g), mp 177—178°, as colorless needles. Mass Spectrum *m/e*: 112 (M^+–16). NMR (CF_3COOH) τ: 6.97 (3H, s, N-$C\underline{H}_3$), 6.06 (3H, s, N–$C\underline{H}_3$), 2.68 (1H, s, a ring proton). *Anal.* Calcd. for $C_4H_8ON_4$: C, 37.49; H, 6.29; N, 43.73. Found: C, 37.59; H, 6.23; N, 43.89.

Photolysis of 5-Chloro-2-benzylidenemethylhydrazinonitrobenzene (IX)——To a solution of 2,5-dichloronitrobenzene (4.0 g) in MeOH (50 ml) was added methylhydrazine (1.5 g) and a small amount of Et_3N in portions. The reaction mixture was heated under reflux for 3 hr. After removal of the solvent, the residue was recrystallized from *n*-hexane to give 5-chloro-2-methylhydrazinonitrobenzene as yellow-orange needles. *Anal.* Calcd. for $C_7H_5O_2N_3Cl$: C, 41.70; H, 4.00; N, 20.84. Found: C, 41.86; H, 4.00; N, 20.80.

To a solution of 5-chloro-2-methylhydrazinonitrobenzene in MeOH containing a catalytic amount of HOAc was added benzaldehyde (0.4 g) in small portions. The mixture was swirled at room temperature for 30 min and evaporated to leave an oily residue. The residue was taken up with $CHCl_3$. The $CHCl_3$ extract was washed with H_2O, dried over anhyd. Na_2SO_4 and evaporated. The residue thus obtained was recrystallized from *n*-hexane to give IX (1.1 g), mp 149°, as yellow-orange crystals. NMR ($CDCl_3$) τ: 2.29—2.83 (9H, m, aromatic protons and an azomethine proton).

A solution of IX (2 g) in benzene (300 ml) was irradiated for 30 hr. After evaporation of the solvent, the residue was chromatographed on silica gel (solvent: $CHCl_3$). Eluant with $CHCl_3$ gave a crystalline mass, which was recrystallized to give 3-methyl-6-chlorobenzotriazole, mp 89—90°, as colorless needles. NMR ($CDCl_3$) τ: 5.69 (3H, s, N–$C\underline{H}_3$), 2.51—2.53 (2H, t, aromatic protons), 1.90 (1H, t, an aromatic proton). *Anal.* Calcd. for $C_7H_6N_3Cl$: C, 50.46; H, 3.63; N, 25.22. Found: C, 50.19; H, 3.71; N, 25.11. A substance remaining on a silica gel column was extracted with $CHCl_3$ under reflux and evaporation of the solvent gave 3-methyl-6-chlorobenzotriazole 1-oxide (X), mp 197°, in 10% yield. NMR (DMSO-d_6) τ: 5.88 (3H, s, N–$C\underline{H}_3$), 1.93—2.87 (3H, m, aromatic protons). *Anal.* Calcd. for $C_7H_6ON_3Cl$: C, 45.79; H, 3.29; N, 22.89. Found: C, 45.92; H, 3.34; N, 22.81. X was identical in every respect with a sample prepared unequivocally as described below.

Synthesis of 3-Methyl-6-chlorobenzotriazole 1-Oxide (X)—— A mixture of 2,5-dichloronitrobenzene (4 g) and hydrazine hydrate (1.5 g) in EtOH containing a small amount of Et_3N was heated under reflux. After removal of an insoluble material by filtration, the filtrate was concentrated and $CHCl_3$ was added to it to deposit a solid mass. The solid thus obtained was recrystallized from EtOH to give hydrazine salt of 6-chlorobenzotriazole 1-oxide (2.7 g), mp 160—161°. *Anal.* Calcd. for $C_6H_8ON_5Cl$: C, 35.75; H, 4.00; N, 34.75. Found: C, 35.75; H, 4.09; N, 36.60. The hydrazine salt was dissolved in EtOH, neutralized with dil. HCl and diluted with H_2O to deposit colorless crystals. Recrystallization from EtOH gave 6-chlorobenzotriazole 1-oxide (XI), mp 193—194°. NMR (DMSO-d_6): 1.84—2.64 (3H, m, aromatic protons). *Anal.* Calcd. for $C_6H_4ON_2Cl$: C, 42.49; H, 2.38; N, 24.78. Found: C, 42.63; H, 2.48; N, 24.96.

A solution of XI in Me_2SO_4 was heated at 100° for 4 hr. After cooling, the reaction mixture was extracted with $CHCl_3$ repeatedly. The $CHCl_3$ extract was dried over anhyd. Na_2SO_4 and evaporated to dryness to leave a solid mass. The solid mass was recrystallized from benzene to give X, mp 197°, as colorless needles.

Photolysis of 2-Phenyl-4-methoxy-5-nitro-6-benzylidenemethylhydrazinopyrimidine (XII)——To a solution of 2-phenyl-4-methoxy-5-nitro-6-chloropyrimidine (4.5 g) in THF (50 ml) was added methylhydrazine (1.6 g) in MeOH (10 ml) with stirring over a period of 2 hr. The reaction mixture was allowed to stand at room temperature to deposit crude 2-phenyl-4-methoxy-5-nitro-6-methylhydrazinopyrimidine, mp about 185°, as a yellow powder. A mixture of crude 2-phenyl-4-methoxy-5-nitro-6-hydrazinopyrimidine (0.25 g) and benzaldehyde (0.2 g) in dioxane (20 ml) was stirred in the presence of AcOH (1—2 drops) for 1 hr at room temperature. The reaction mixture was then concentrated under reduced pressure, and the residue was purified by Florisil chromatography (solvent: $CHCl_3$) and recrystallized from MeOH to give XII (0.25 g) as yellow prisms, mp 200°. *Anal.* Calcd. for $C_{19}H_{17}O_3N_5$: C, 62.80; H, 4.72; N, 19.28. Found: C, 62.35; H, 4.60; N, 18.99.

A solution of XII (0.25 g) in benzene (100 ml) was irradiated for 8 hr. The irradiated solution was concentrated under reduced pressure, and the residue was purified by silica gel chromatography (solvent: $CHCl_3$) and recrystallized from acetone to give 3-methyl-5-phenyl-7-methoxytriazolo(4,5-*d*)pyrimidine 1-oxide (XIII), mp 228°, as colorless needles in 50% yield. *Anal.* Calcd. for $C_{12}H_{11}O_2N_5$: C, 56.02; H, 4.31; N, 27.23. Found: C, 55.52; H, 4.33; N, 27.11. XIII was easily reduced to 3-methyl-5-phenyl-7-methoxytriazolo(4,5-*d*)pyrimidine, mp 178—179°, upon treatment with sodium hydrosulfite. *Anal.* Calcd. for $C_{12}H_{11}O_2N_5$: C, 59.74; H, 4.60; N, 29.03. Found: C, 59.61; H, 4.90; N, 29.78. NMR ($CDCl_3$) τ: 1.4—2.7 (5H, m, aromatic protons), 5.73 (3H, s, $OC\underline{H}_3$), 6.04 (3H, s, $N-C\underline{H}_3$). Mass Spectrum *m/e*: 241 (M^+).

Photolysis o 2-Benzylidene (or Acetophenylidene) methylhydrazino-3-nitropyridine (XIVa,b)——A mixture of 2-chloro-3-nitropyridine (1.6 g) and methylhydrazine (1.2 g) in EtOH (15 ml) was stirred for 2 hr at room temperature. The reaction mixture was concentrated under reduced pressure to remove an excess of methylhydrazine. The resulting residue was dissolved in EtOH (20 ml) and to this solution added benzaldehyde (1.6 g) and AcOH (1—2 drop). The mixture was then refluxed for 1 hr, concentrated under reduced pressure, submitted to steam distillation to remove an excess of benzaldehyde, and extracted with $CHCl_3$. The $CHCl_3$ extract was concentrated and recrystallized from MeOH to give XIVa (1.5 g) as yellow prisms, mp 107—108°. *Anal.* Calcd. for $C_{13}H_{12}O_2N_4$: C, 60.93; H, 4.72; N, 21.87. Found: C, 60.81; H, 4.71; N, 22.13. In a similar manner, XIVb, mp 113°, was obtained by the reaction of the crude 2-methylhydrazino-3-nitropyridine with acetophenone. *Anal.* Calcd. for $C_{14}H_{14}O_2N_4$: C, 62.11; H, 5.22; N, 20.73. Found: C, 61.96; H, 5.23; N, 20.86.

A solution of XIVa (0.5 g) in acetone (100 ml) was irradiated for 12 hr. The irradiated solution was concentrated under reduced pressure and submitted to silica gel chromatography (solvent: $CHCl_3$). The first eluent gave unchanged XIVa (0.28 g). The second eluent was recrystallized from EtOH to give 3-methyltriazolo(4,5-*b*)pyridine 1-oxide (XV) (0.09 g, 35%) as colorless needles, mp 214°. *Anal.* Calcd. for $C_6H_6ON_4$: C, 48.00; H, 4.03; N, 37.37. Found: C, 47.81; H, 4.09; N, 37.18. NMR ($CDCl_3$) τ: 1.20 (1H, d of d, $J_{4,6}=1.5$ Hz, $J_{5,6}=5$ Hz, C_6–H), 1.63 (1H, d of d, $J_{4,6}=1.5$ Hz, $J_{4,5}=8.5$ Hz, C_4–H), 2.57 (1H, d of d, $J_{5,6}=5$ Hz, $J_{4,5}=8$ Hz, C_5–H), 5.79 (3H, s, $N-CH_3$). Mass Spectrum *m/e*: 150 (M^+, base peak), 134 (M^+-16).

A solution of XIVb (0.5 g) in acetone (100 ml) was irradiated for 8 hr. The irradiated solution was concentrated under reduced pressure, and the residue was purified by silica gel chromatography (solvent: $CHCl_3$) and recrystallized from EtOH to give XV (0.17 g, 62%), identical in every respect with a specimen obtained above.

Acknowledgement This work was supported by the Grant for Scientific Research from the Ministry of Education. The authors are grateful to the stuff of microanalytical room of this college for elemental analyses.