

Photochemical Reactions. Part 21.¹ Photochemical Isomerization of Pyridazinium and Triazinium Betaines²

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Irradiation of 5-oxidopyridazinium betaines (1) results in the smooth isomerization leading to pyrimidin-4(3*H*)-ones (2). When 1-oxidophthalazinium betaine (6) and 3-oxidopyridazinium betaine (11) are photolysed in water, the corresponding phthalazin-1(2*H*)-one (8) and pyridazin-3(2*H*)-one (13) are isolated in high and low yields, respectively. Upon employment of acetonitrile instead of water as solvent, irradiation of the betaines (6) and (11) gives the stable fused diaziridines (7) and (12) which are converted easily into the phthalazin-1(2*H*)-one (8) and pyridazin-3(2*H*)-one (13) by the action of water. Photolysis of 4-oxido-1,2,3-benzotriazinium betaines (15) causes photoisomerization to give benzotriazin-4(3*H*)-ones (16) in high yields.

THE photochemistry of five-membered heterocyclic systems, which can only be represented by dipolar structures and are termed as mesoionic, has been extensively investigated.³ The photoreactions observed in these five-membered mesoionic heterocycles may be rationalized in terms of their initial valence-isomerization to bicyclic systems followed by fragmentation.†

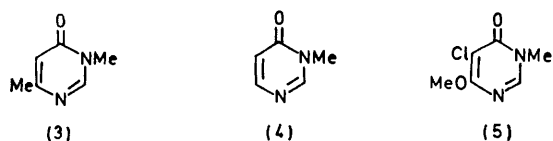
Recently, much attention has been directed toward six-membered mesoionic heterocycles, which are essentially mesomeric betaines with aromatic character,⁵ because of their participation in 1,3-dipolar cycloaddition⁶ similar to the five-membered mesoionic heterocycles.

Prior to our preliminary publication² of part of this work, however, there had been no report concerning the photochemistry of six-membered mesoionic heterocycles except for photochemical ring-contraction of the fused-pyridazinium betaines.⁷ More recently, some observations in the photoisomerization of pyridinium betaines⁶ and fused-pyridazinium betaines have been accumulated.^{8,9}

Here, we describe in full detail the photochemical behaviour observed in 5-oxidopyridazinium, 1-oxidophthalazinium, 3-oxidopyridazinium, and 4-oxidobenzotriazinium betaines.



- (1) a: R¹ = Me R² = CH₂OH R³ = H d: R¹ = *p*-MePh R² = CH₂OH R³ = H
 b: R¹ = Ph R² = CH₂OH R³ = H e: R¹ = Me R² = R³ = Cl
 c: R¹ = *p*-ClC₆H₄ R² = CH₂OH R³ = H f: R¹ = Me R² = Cl R³ = OMe



SCHEME 1

Photochemistry of 5-Oxidopyridazinium Betaines (1).—5-Oxidopyridazinium betaines (1a—d) were conveniently prepared by condensation of calcium 2,5-dioxogluconate

with monosubstituted hydrazines.¹⁰ 3,4-Dichloro-1-methyl-5-oxidopyridazinium betaine (1e) was obtained in 60% yield by refluxing a mixture of 3,4-dichloro-5-

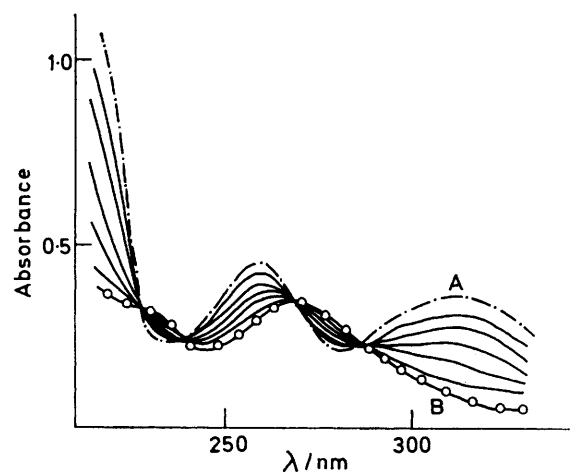


FIGURE 1 U.v. spectral changes of the 3-hydroxymethyl-1-methyl-5-oxidopyridazinium betaine (1a) in ethanol during irradiation with 338 nm light at room temperature: A, (1a); B, 6-hydroxymethyl-3-methylpyrimidin-4(3*H*)-one (2a)

hydroxypyridazine and dimethyl sulphate in toluene.¹¹ 3-Chloro-4-methoxy-1-methyl-5-oxidopyridazinium betaine (1f) was prepared by reaction of 3-chloro-5-hydroxy-4-methoxypyridazine with methyl iodide in dimethylformamide.

A solution of the betaine (1a—d) in ethanol was irradiated with a high-pressure mercury arc lamp through a Pyrex filter under nitrogen at room temperature until disappearance of the starting material was completed. The irradiated solution was concentrated and the residue was purified by recrystallization or, if necessary, by silica-gel chromatography to obtain the 3-substituted-6-hydroxymethylpyrimidin-4(3*H*)-ones (2a—d) in moderate to high yield.

The u.v. spectrum of (1a) in ethanol during the irradiation showed a gradual change with four isosbestic points, indicating a stoichiometric relation in the formation of (2a) from (1a) (see Figure 1). The low yield of

† Only a few examples of the photoisomerization, in which two atoms in the heterocyclic ring simply exchange their positions, have been reported in the five-membered mesoionic system.⁴

N-phenylpyrimidinones (2b—d) in comparison with *N*-methylpyrimidinone (2a) may be ascribed to the greater light sensitivity of the former which causes further photoreactions. Changes of the n.m.r. and u.v. spectra of (1b) during the irradiation accommodated to this aspect.

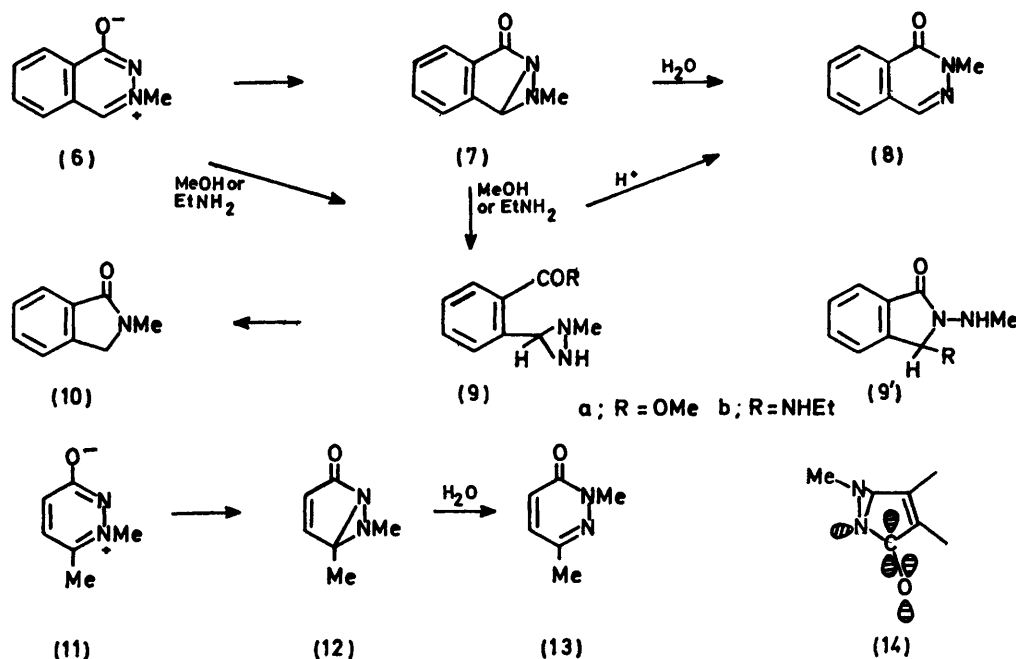
All photoproducts (2a—d) showed u.v. absorption bands characteristic of 3-substituted pyrimidin-4(3*H*)-ones; e.g. the u.v. spectrum of (2a) in ethanol [λ_{max} (ϵ): 224 (5 600) and 270 nm (3 400)] is similar to that of 3,6-dimethylpyrimidin-4(3*H*)-one (3)¹² [λ_{max} (ϵ): 224 (5 600) and 268 nm (3 600)]. Transformation of (2a) into the corresponding pyrimidinone (3) by refluxing with Raney nickel in ethanol confirmed its structure.

of their toluene-*p*-sulphonates with ion-exchange resin according to a previously reported procedure.¹⁴

Irradiation of the betaine (6) in water with a high-pressure mercury arc lamp gave 2-methylphthalazinone (8) in nearly quantitative yield. The photoproduct (8) was identical in every respect with a sample prepared independently.¹⁴

When the betaine (6) was irradiated in dry acetonitrile instead of water, no formation of the expected phthalazinone (8) was observed. Monitoring by the n.m.r. spectroscopy showed the presence of an intermediary photoproduct which underwent further photoreactions during the irradiation.

Isolation of the intermediary photoproduct formed by



SCHEME 2

Analogously, the betaines (1e) and (1f) underwent photoisomerization to 5,6-dichloro-3-methylpyrimidin-4(3*H*)-one (2e) and 6-chloro-5-methoxy-3-methylpyrimidin-4(3*H*)-one (2f) almost quantitatively. Structural proof of (2e) follows from its transformation into 3-methylpyrimidin-4(3*H*)-one (4) by catalytic dechlorination.¹³ It was proved that the pyrimidinone (5) was prepared by reaction of the 5,6-dichloropyrimidinone (2e) with sodium methoxide.

More recent studies^{8,9} have demonstrated analogous photoisomerization of fused 5-oxopyridazinium betaines leading to fused pyrimidin-4(3*H*)-ones. Thus, this type of photoisomerization is general for the 5-oxopyridazinium betaine system, regardless of the nature of the substituents at various positions of the pyridazine ring.

Photochemistry of 1-Oxidophthalazinium and 3-Oxopyridazinium Betaines (6) and (11).—3-Methyl-1-oxidophthalazinium betaine (6) and 1,6-dimethyl-3-oxopyridazinium betaine (11) were prepared upon treatment

the irradiation in acetonitrile was achieved simply by removal of the solvent under reduced pressure immediately after the disappearance of (6). Irradiation experiments using a monochromator showed that the formation of the photoproduct is cleanly completed after a short period and employment of long wavelength light (360—390 nm) as a light source prevented further photoreactions of the photoproducts. The irradiation of (6) in acetonitrile using 391 nm light showed the gradual change of the u.v. spectrum of (6) with four isobestic points, while the irradiation with 285 nm light caused the u.v. spectral change without isobestic points (see Figure 2).

The purity of the oily photoproducts thus obtained was satisfactory for its characterization and further studies on its reactions.

The spectral data of the oily photoproduct were consistent with the structure of tricyclic fused-diaziridine (7); i.r. spectrum (KBr) 1 750 cm^{-1} (CO); n.m.r. spectrum (CDCl_3) δ 2.79 (NMe), 4.23 (a bridge-head

proton), and 7.24–7.87 (ArH); u.v. spectrum (MeCN) λ 250 and 290 nm. Treatment of (7) with methanol or aqueous ethylamine at room temperature resulted in the formation of *o*-(1-methyldiaziridin-3-yl)benzoic acid methyl ester or ethylamide [(9a) oil or (9b) m.p. 77 °C] in ca. 90% yields, respectively. Photolysis of (6) in methanol or aqueous ethylamine gave directly (9a) or (9b) in high yield as a result of trapping of the intermediary photoproduct (7).

The alternative structure (9a') or (9b') can be eliminated on the basis of their spectral data and chemical reactions; *i.e.* the i.r. spectrum of (9b) showed an amide carbonyl band at 1 640 cm^{-1} ; catalytic hydrogenation of (9a) over palladium-charcoal gave *N*-methylphthalimidine (10) in 50% yield, which can be formed *via* reductive cleavage of the diaziridine ring accompanied by loss of ammonia and subsequent cyclization.¹⁵ Treatment of (9a) and (9b) with trifluoroacetic acid caused the smooth conversion into (8).

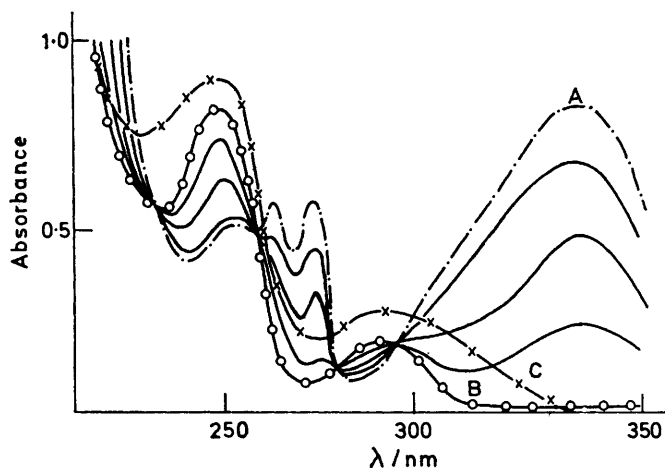


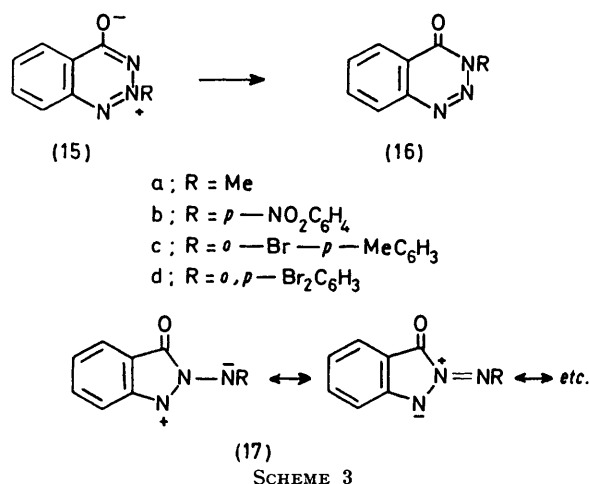
FIGURE 2 U.V. spectral changes of 3-methyl-1-oxidophthalazinium betaine (6) in acetonitrile during irradiation with 391 nm light at room temperature: A, (6); B, fused diaziridine (7); C, a mixture of photoproducts obtained finally after irradiation with 285 nm light

The fused diaziridine (7) was transformed with ease into (8) when it was set aside in acetonitrile containing a small amount of water at room temperature in the dark. This conversion was significantly accelerated by addition of trifluoroacetic acid.

Analogously, the irradiation of the pyridazinium betaine (11) in acetonitrile gave the fused diaziridine (12) as an oil. Structure (12) was fully supported by spectral data, *i.e.* i.r. spectrum (KBr) 1 745 cm^{-1} (C=O); n.m.r. spectrum (CDCl_3) δ 1.72 (CMe), 2.68 (NMe), and 5.78 and 7.57 (AB-type quartet, vinyl protons); mass spectrum $M^+ m/e = 124$. Conversion of (12) into 2,6-dimethylpyridazin-3(2H)-one (13) was observed upon treatment with water at room temperature. Photolysis of (11) in water, however, afforded 2,6-dimethylpyridazin-3(2H)-one (13) only in low yield together with other undetermined products.

The above experiments showed that the amide bond of

the fused diaziridines (7) and (12) is sensitive to hydrolysis, aminolysis, and alcoholysis, behaviour which can



be explained in terms of reduced amide resonance as a result of inefficient overlapping between the *p*-orbital of the bridge-head nitrogen and the π -orbital of the carbonyl group in (7) and (12) [see (14) in Scheme 2]. The high-frequency amide carbonyl bands observed in the spectra of these compounds support this explanation.¹⁶

Thus, the photoconversion of the betaines (6) and (11) into the pyridazinones (8) and (13) in water was proved to involve hydrolysis of the initially formed fused diaziridines (7) and (12). The inefficient photoconversion of (11) into (13) in water may be ascribed to the greater photosensitivity of the intermediate (12) compared with (7).

Further studies on the photochemistry of the fused diaziridines (7) and (12) in the absence of any nucleophile are now in progress.

Photochemistry of 2-Substituted 4-Oxido-1,2,3-benzo-

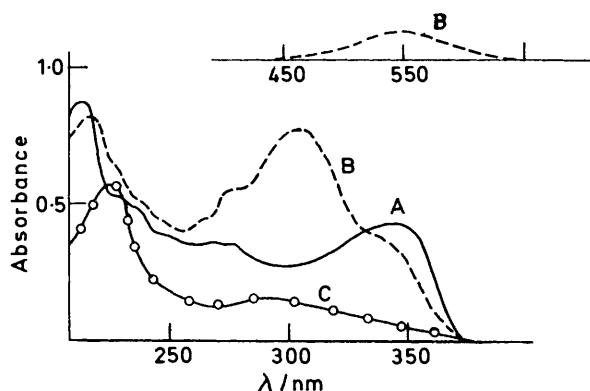


FIGURE 3 U.V. spectral changes of 2-(*o*-bromotolyl)-4-oxido-1,2,3-benzotriazinium betaine (15c) in acetonitrile during irradiation with 338 nm light at room temperature: A, (15c); B, intermediate product; C, 3-(*o*-bromotolyl)-1,2,3-benzotriazin-4(3H)-one (16c)

triazinium Betaines (15).—2-Phenylbenzotriazinium betaines (15b–c) were prepared by base treatment of the

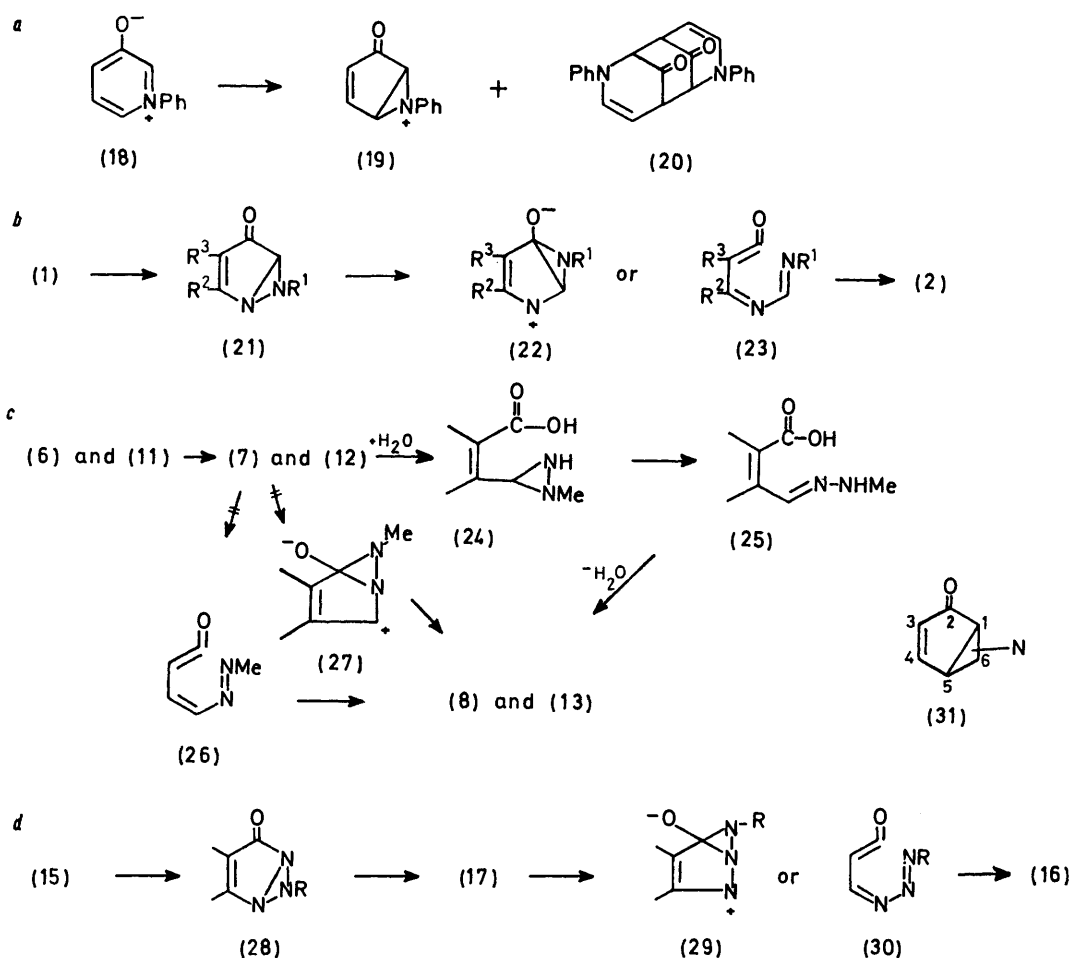
corresponding *N*-phenyl-2-nitrobenzhydrazonoyl bromides followed by reduction.¹⁷⁻²⁰ 2-Methylbenzotriazin-ium betaine (15a) was obtained by methylation of 1,2,3-benzotriazin-4(3*H*)-one with dimethyl sulphate.²⁰

Irradiation of the betaines (15a-d) in acetonitrile was carried out under the conditions similar to the cases of pyridazinium betaines. The corresponding 3-substituted 1,2,3-benzotriazin-4(3*H*)-ones (16a-d) were obtained almost quantitatively.

The structures of (16a-d) were fully supported by

sense of isomerization during the photolysis of 2-(*p*-dimethylaminophenyl)-4-oxido-1,2,3-benzotriazin-ium (15; R = *p*-dimethylaminophenyl) in dichloromethane.²²

Photofragmentation of 3-phenyl-1,2,3-benzotriazin-4(3*H*)-one (16; R = Ph) accompanied by loss of nitrogen has been extensively studied.²³ Upon further irradiation of (16a) for 3 h under the conditions employed at present, however, no appreciable gas evolution was observed and the starting material (16a) was recovered unchanged.



SCHEME 4

physicochemical data and microanalytical results. The independent synthesis of the *p*-nitrophenyl derivative (16b) confirmed its structure.²¹

The u.v. spectrum of (15c) during the irradiation showed the characteristic absorption bands (305 and 550 nm), which disappear on heating, in the intermediate stage (see Figure 3). The final u.v. spectrum is quite similar to that of the benzotriazinone (16c). The absorption bands in the intermediate stage appear to arise from the formation of a stable dipolar azimine species (17),¹⁹ presumably being an intermediate leading to the benzotriazin-4(3*H*)-ones (16).

These results are in contrast with the reported ab-

DISCUSSION

Recently, Dennis, Katritzky, and Wilde⁶ have reported that irradiation of 3-oxido-1-phenylpyridinium (18) gives a fused aziridine (19) in crystalline form together with a symmetrical dimer (20) (see *a* in Scheme 4). It has been also demonstrated that the fused aziridine (19) undergoes both further thermal addition to the starting betaine (18) and photoreactions.

Irradiation of the 3-oxidopyridaziniums (6) and (11) in water resulted in the formation of pyridazin-3(2*H*)-ones (8) and (13). The experimental facts clearly showed that the isomerization involves hydrolysis of the weak amide bond of the initially formed diaziridines (7) and

(12) to carboxylic acids (24). Subsequently, ready cleavage of the diaziridine ring of the carboxylic acids (24) can be accounted for by the participation of a carboxylic proton. Cyclization of the resulting hydrazones (25) could give the rearranged products (8) and (13). Acceleration of the rearrangement of (7) and (12) by addition of acids is relevant to the above process. In this case, photoisomerization involving a keten or zwitterionic intermediate (26) or (27) can be undoubtedly excluded (see *c* in Scheme 4).

The fused diaziridine (12) appears to be more unstable than its benzo-analogue (7) and to undergo further reactions in analogy with the fused aziridine (19) formed from the pyridinium betaine (18).⁶

On the other hand, 5-oxidopyridaziniums (1) isomerized smoothly to the corresponding pyrimidin-4(3H)-ones (2). In a manner similar to the cases described above, it is believed that the fused diaziridine (21) is formed by a photochemically allowed disrotatory closure of (1) in the initial stage of the reaction. The diaziridine (21) could undergo ready N-N bond cleavage photochemically or thermally to give a zwitterionic or keten

both the 5- and 6-positions of the bicyclic system (31) such as (21) and (28) appears to be requisite for the subsequent rearrangement *via* a keten or zwitterionic intermediate.

Although various fused diaziridines have been proposed as an intermediate in the photoisomerization of some heterocycles,* only 6-phenyl-1,5-diazabicyclo-[3.1.0]hexane has been isolated upon irradiation of 1-benzylidene-3-oxidopyrazolidium betaine.¹⁶ From this point of view, isolation of the new fused diaziridines (7) and (12) in the irradiation of 3-oxidopyridazinium betaines (6) and (11) is of special interest.

EXPERIMENTAL

I.r. spectra were recorded with a Hitachi 215 spectrometer for potassium bromide discs and ¹H n.m.r. spectra with a Hitachi R-20B 60 MHz spectrometer for solution in deuteriochloroform or deuteriodimethyl sulphoxide containing tetramethylsilane as internal standard. Mass spectra were measured at 75 eV with a JEOL JMS-OISG spectrometer and u.v. spectra with a Shimadzu MPS-50L spectrophotometer for solutions in ethanol. Column chromatography was performed on silica gel (Mallinckrodt;

TABLE I
3-Substituted 6-hydroxymethylpyrimidin-4(3H)-ones (2a—d)

	M.p. (°C)	Yield (%) (solvent)	Found (%)			Formula	Required (%)		
			C	H	N		C	H	N
(2a)	118	75 (benzene)	51.3	5.8	19.95	C ₈ H ₈ N ₂ O ₂	51.42	5.75	19.99
(2b)	201	55 (ethanol)	65.1	5.0	13.85	C ₁₁ H ₁₀ N ₂ O ₂	65.33	4.98	13.86
(2c)	185	35 (ethanol)	56.0	3.9	12.1	C ₁₁ H ₉ N ₂ O ₂ Cl	55.82	3.83	11.84
(2d)	203	40 (ethanol)	66.9	5.65	13.1	C ₁₁ H ₁₂ N ₂ O ₂	66.65	5.59	12.96

intermediate (22) or (23) leading to the pyrimidinones (see *b* in Scheme 4).

In the photoisomerization of the 4-oxidotriaziniums (15), the fused triaziridine (28) could be initially produced and give stepwise a zwitterionic or keten intermediate (29) or (30) *via* a dipolar azimine species (17) (see *d* in Scheme 4).

Subsequent photoisomerization of the fused aziridine (19) to the corresponding pyridones has not been observed.⁶ Although the reversible photochemically-allowed valence isomerizations between isoquinolinium betaines and fused aziridines have been reported,^{24,25} the conversion of the fused aziridines into isoquinolinones is also unknown.

The results available indicate that the six-membered mesoionic heterocycles undergo photochemically-allowed disrotatory ring closure to give the azabicyclo-[3.1.0]hex-3-en-2-ones (31) and their further reactions depend largely upon the position of the nitrogen in the bicyclic system (31). The presence of the nitrogen in

* For example, J. M. Cassel and J. Streith, *Tetrahedron Letters*, 1976, 4859. Recently, the photoconversion of 2,3-dimethylindazole into 1,2-dimethylbenzimidazole has been shown to proceed *via* the detectable fused diaziridine intermediate by irradiation (300 nm) at -60 °C (W. Heinzelmann, M. Marky, and P. Gilgen, *Helv. Chim. Acta*, 1976, **59**, 1512).

100 mesh) using chloroform as eluant. Irradiations were performed with a Rikoshia 100W high-pressure mercury arc lamp through a Pyrex filter under nitrogen. A JASCO GRM-FA radiating monochromator (2 kW Xenon arc lamp) was used for monochromatic light irradiation. Reagent grade benzene and acetonitrile were redistilled prior to use as solvent.

Photoisomerization of 1-Substituted 3-Hydroxymethyl-5-oxidopyridaziniums (1a—d).—A solution of each of the betaines (1a—d) (0.3 g) in ethanol (100 ml) was irradiated with a 100W high-pressure mercury arc lamp at room temperature until disappearance of (1a—d) was complete. The reaction was monitored by thin-layer chromatography and by taking n.m.r. and u.v. spectra. The irradiated solution was concentrated under reduced pressure and the residue was purified by recrystallization or, if necessary, by silica-gel chromatography (solvent: chloroform-methanol 20 : 1) to obtain the 3-substituted 6-hydroxymethylpyrimidin-4(3H)-ones (2a—d): (2a), *m/e* 140 (*M*⁺), λ_{max} (ε) 224 (5 600), and 270 nm (3 400), δ [(CD₃)₂SO] 3.40 (3 H, s, NMe), 4.28 (2 H, d of d, *J*₁ = 1.5 Hz, *J*₂ = 5.5 Hz, CH₂), 5.45 (1 H, t, *J* = 5.5 Hz, OH, deuterium exchangeable), 6.38 (1 H, d of d, *J*₁ = 1 Hz, *J*₂ = 1.5 Hz, 5-H), 9.40 (1 H, d, *J* = 1 Hz, 2-H), ν_{max} 3 250 (OH) and 1 680 cm⁻¹ (CO).

Refluxing (2a) with Raney nickel in ethanol for 5 h gave 3,6-dimethylpyrimidin-4(3H)-one (3)¹² [λ_{max} (ε) 224 (5 600) and 268 nm (3 600)] in 50% yield.

Photoisomerization of 3,4-Dichloro-1-methyl (and 3-Chloro-4-methoxy)-5-oxidopyridaziniums (1e and f).—A mixture of 3,4-dichloro-5-hydroxypyridazine (5g) and dimethyl sulphate (4g) in toluene (150 ml) was heated under reflux for 4 h. After cooling, an oily substance was separated by decantation and triturated with water to give 3,4-dichloro-5-oxidopyridazinium (1e) (55%) as colourless crystals, m.p. 217 °C (Found: C, 35.55; H, 2.40; N, 15.52. $C_5H_4Cl_2ON_2$ requires C, 35.75; H, 2.24; N, 15.64), ν_{max} 3 025, 1 615 and 1 580 cm^{-1} ; $\delta(CD_3OD)$ 4.26 (3 H, s, Me) and 8.52 (1 H, s, a ring proton); λ_{max} (ϵ) 273 (5 200) and 324 nm (6 200).

Analogous irradiation of (1e) in methanol gave 5,6-dichloro-3-methylpyrimidin-4(3H)-one (2e) (95%) as colourless crystals, m.p. 108 °C. The pyrimidinone (2e) thus obtained was dechlorinated by catalytic reduction (palladium-carbon) to give 3-methylpyrimidin-4(3H)-one (4) which was identical in every respect with an authentic sample.¹³

When 3-chloro-5-hydroxy-4-methoxypyridazine was heated with methyl iodide in dimethylformamide, the pyridazinium betaine (1f) was obtained as colourless crystals (60%, 221°) λ_{max} (ϵ) 328 nm (4 400). The n.m.r. spectral changes of (1f) during the irradiation in an n.m.r. tube in deuteriomethanol shows the quantitative conversion into 6-chloro-5-methoxy-3-methylpyrimidin-4(3H)-one (2f), δ

The conversion of (9a) into the phthalazinone (8) occurred with ease upon treatment with trifluoroacetic acid.

(c) *Photolysis in 70% aqueous ethylamine.* The betaine (6) (1 g) in 70% aqueous ethylamine (200 ml) was irradiated under the analogous conditions for ca. 5 h. The irradiated solution was taken up with chloroform. The organic layer was washed with water, dried, and concentrated under reduced pressure. The residue was recrystallized from ether-ethanol to give *o*-(1-methyldiaziridin-3-yl)benzoic acid ethylamide (9b) (80%), m.p. 77 °C, as colourless crystals (Found: C, 64.1; H, 7.35; N, 20.3. $C_{11}H_{15}N_3O$ requires C, 64.36; H, 20.47; N, 7.37), ν_{max} 3 350 (NH) and 1 640 cm^{-1} (CO); λ_{max} 278 nm; m/e 204 ($M^+ - 1$); $\delta(CDCl_3)$ 2.54 (3 H, s, NMe), 3.68 (1 H, s, CH), 6.55 (1 H, m, NH), and 7.25 (4 H, m, ArH). Reaction of (9b) with trifluoroacetic acid resulted in the formation of the phthalazinone (8).

(d) *Photolysis in acetonitrile.* The betaine (6) (1g) in acetonitrile (300 ml) was irradiated under analogous conditions for ca. 3 h. The irradiated solution was concentrated under reduced pressure to leave 8-methyl-2,3-epimino-isoindol-1(2H)-one (7) as an oil, ν_{max} 1 750 cm^{-1} (CO), λ_{max} (MeCN) 249 and 291 nm; m/e 160 (M^+), $\delta(CDCl_3)$ 2.79 (3 H, s, NMe), 4.23 (1 H, s, a methine proton), and 7.24–7.84 (4 H, m, ArH).

When the fused diaziridine (7) was set aside in water,

TABLE 2
3-Substituted 1,2,3-benzotriazin-4(3H)-ones (16a–d)

	M.p. (°C)	Yield (%)	Found (%)			Formula	Required (%)		
			C	H	N		C	H	N
(16a)	123	75	59.6	4.3	25.95	$C_8H_7N_3O$	59.62	4.38	26.07
(16b)	254	70	58.1	3.05	20.9	$C_{13}H_8N_3O_2$	58.21	3.01	20.89
(16c)	185	80	52.95	3.15	13.4	$C_{14}H_{10}N_3OBr$	53.17	3.17	13.29
(16d)	189	85	41.0	1.85	11.1	$C_{13}H_7N_3OBr_2$	40.94	1.84	11.02

3.54 (3 H, s, NMe), and 3.97 (3 H, s, OMe). The n.m.r. spectrum of (2f) was distinguished from that of the isomeric pyrimidinone (5), $\delta(CD_3OD)$ 3.56 (3 H, s, NMe) and 4.01 (3 H, s, OMe), which was prepared by reaction of the 5,6-dichloro-3-methylpyrimidin-4(3H)-one (2e) with sodium methoxide.

Photolysis of 3-Methyl-1-oxidophthalazinium (6).—(a) *Photolysis in water.* The 1-oxidophthalazinium (6) (3g) in water (200 ml) was irradiated with a 100W high-pressure mercury lamp for 10 h. The irradiated solution was extracted with chloroform and the organic layer was concentrated under reduced pressure to dryness. The solid residue was recrystallized from ethanol to give 2-methylphthalazin-1(2H)-one (8) (90%) as colourless crystals, m.p. 116 °C (Found: C, 67.6; H, 5.0; N, 17.65. $C_8H_8N_2O$ requires C, 67.50; H, 5.00; N, 17.80), ν_{max} 1 630 cm^{-1} (CO); λ_{max} (ϵ) 287 nm (10 700); $\delta[(CD_3)_2SO]$ 3.71 (3 H, s, NMe), 8.31 (1 H, s, N=CH), and 7.65–8.30 (4 H, m, ArH). The phthalazinone (8) thus obtained was identical in every respect with an authentic sample prepared by methylation of phthalazin-1(2H)-one (methyl iodide-anhydrous Na_2CO_3 in dimethylformamide).

(b) *Photolysis in methanol.* The betaine (6) (1g) in methanol (300 ml) was irradiated under the analogous conditions for ca. 2 h. After removal of the solvent, the residue was chromatographed on silica gel to give *o*-(1-methyldiaziridin-3-yl)benzoic acid methyl ester (9a) (70%) as an oil, ν_{max} 3 250 (OH) and 1 720 cm^{-1} (CO); λ_{max} 279 nm; m/e 191 ($M^+ - 1$); $\delta(CDCl_3)$ 2.10br (1 H, NH), 2.62 (3 H, s, NMe), 3.90 (3 H, s, OMe), and 4.03 (1 H, s, a methine proton).

methanol, or 70% aqueous ethylamine at room temperature, the phthalazinone (8), the methyl ester (9a), or the ethylamide (9b) was obtained in high yield. These conversions were accelerated by slight warming or addition of acids.

Photolysis of 1,6-Dimethyl-3-oxidopyridazinium (11).—A solution of the betaine (11) (1g) in acetonitrile (200 ml) was irradiated with a 100W high-pressure mercury lamp. After disappearance of the betaine (11) was complete (monitored by t.l.c.), the solution was concentrated under reduced pressure to leave 5,6-dimethyl-1,6-diazabicyclo-[3.1.0]hex-3-en-2-one (12) as an oil, ν_{max} 1 745 cm^{-1} (CO); $\delta(CDCl_3)$ 1.72 (3 H, s, Me), 2.68 (3 H, s, NMe), and 5.78 and 7.57 (each 1 H, an AB-type quartet, $J = 5.5$ Hz, vinyl protons); m/e 124 (M^+). Conversion of (12) into 2,6-dimethylpyridazin-3(2H)-one (13) was observed upon treatment with water at room temperature. The pyridazinone (13) was identical in every respect with an authentic sample.

Irradiation of the betaine (11) in water under analogous conditions resulted in the formation of the pyridazinone (13) in 25% yield. The presence of other undetermined products in the reaction mixture was detected by t.l.c.

Photoisomerization of 2-Substituted 4-Oxido-1,2,3-benzotriaziniums (15a–d).—A solution of each of the betaines (15a–d) (0.5 g) in acetonitrile (300 ml) was irradiated with a 400 W high-pressure mercury lamp. After disappearance of (15a–d) was complete (monitored by t.l.c.), the solution was concentrated under reduced pressure. The residue was chromatographed on silica gel and recrystallized from

ethanol to give the 3-substituted 1,2,3-benzotriazin-4(3H)-ones (16a—d).

A part of this work was supported by the grant-in-aid for Scientific Research from the Ministry of Education, Science and Culture of Japan. We are grateful to Dr. K. Imada, Daiichi Pharmaceutical Company Ltd., for supplying some of 5-oxidopyridazinium betaines.

[8/216 Received, 9th February, 1978]

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