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PHOTOCHEMISTRY OF 3-OXIDOPYRIDAZINIUM BETAINES[1]
ISOLATION AND REACTION OF NEW FUSED DIAZIRIDINES

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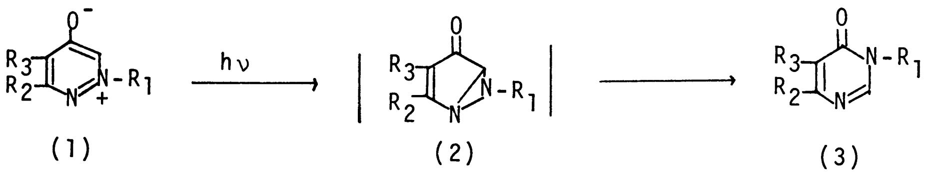
Irradiation of 3-oxidopyridazinium betaines(4) and (9) in acetonitrile gave fused diaziridines(5) and (10) which are stable enough to isolate. The amido bond of (5) underwent alcoholysis and aminolysis with ease. Thus, apparent phototranspositions of (4) and (9) to pyridazinones(6) and (11) in water were proved facile hydrolysis of the amide bonds of the intermediates(5) and (10).

A previous article[2] from our laboratory described the facile phototransposition of 5-oxidopyridazinium betaines(1) to 4(3H)-pyrimidones(3) presumably *via* a fused diaziridine intermediate(2). This type of phototransposition was also observed in fused derivatives of the betaines.[3]



Scheme 1

This paper describes the photochemical behavior of 1-methyl-3-oxidophthalazinium(4)[4] and 1,6-dimethyl-3-oxidopyridazinium(9)[4] which is hitherto unknown.

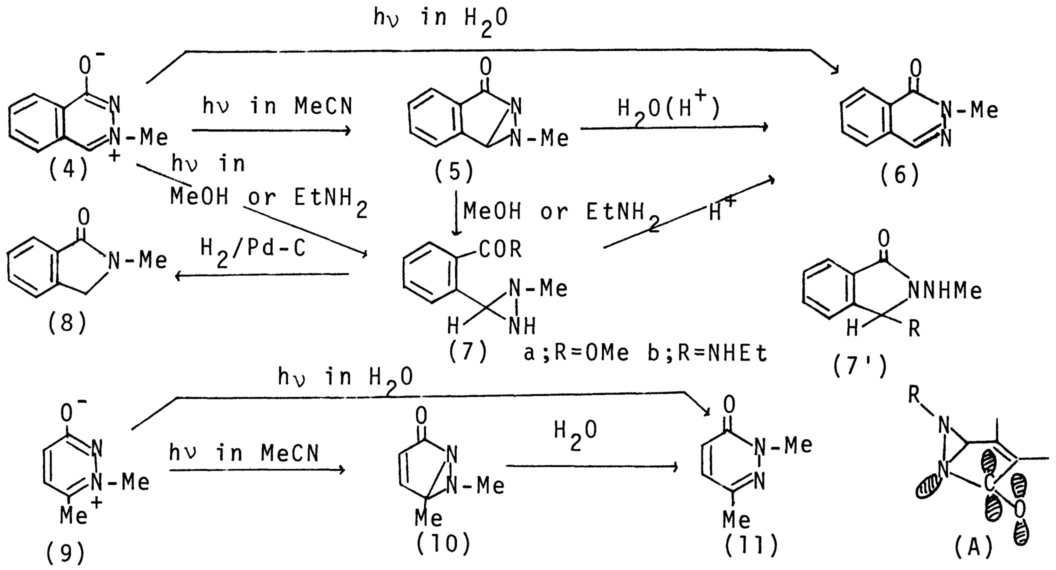
Significant observations in the present study are concerned with isolation, characterization and reaction of new fused diaziridines, 1,6-diazabicyclo[3:1:0]-hex-3-ene-2-one derivatives(5) and (10), produced photochemically from (4) and (9). Consequently, the apparent phototranspositions of (4) and (9) to pyridazinone derivatives(6) and (11) *in water* were proved to involve facile hydrolysis of the amide bonds in the intermediates(5) and (10).

Irradiation of (4) in water by a 400W high-pressure mercury arc lamp through a Pyrex filter under nitrogen gave ultimately 2-methylphthalazinone(6) in nearly quantitative yield. Analogous photolysis of (9) in water, however, gave 3(2H)-pyridazinone(11) in low yield together with other undetermined products.

When (4) was irradiated in dry acetonitrile instead of water, no formation of the expected (6) was observed. Monitoring by the NMR spectroscopy showed the presence of an intermediary photoproduct which subsequently underwent complicated photoreactions.

Isolation of the intermediate formed by the irradiation in acetonitrile was attained simply by removal of the solvent under reduced pressure immediately after the disappearance of (4). Irradiation experiments using a monochrometer showed that the formation of the intermediate completed cleanly during a short period and employment of a long wave-length light(360-390 nm) as a light source allowed to prevent further photoreactions of the intermediate.

The purity of the oily photoproduct thus obtained was satisfactory for its characterization and further studies on its reactions[mass spectrum m/e M^+=160; Ir spectrum(KBr, cm^{-1}) 1750 C=O; NMR spectrum($CDCl_3$,δ) 2.79 NCH_3, 4.23 a bridgehead proton, 7.24-7.87 phenyl protons; UV spectrum(MeCN, nm) 250, 290].



Scheme 2

Treatment of (5) with methanol or aqueous ethylamine at room temperature resulted in the formation of o-(1-methyl-3-diaziridinyl)benzoic acid derivatives (7a; oil and 7b; mp 77°)5)in 90% yields, respectively. Photolysis of (4) in methanol or aqueous ethylamine gave directly (7a)or(7b) in high yield as a result of trapping of the intermediate(5).

The alternative structures(7'a and b) can be eliminated on the basis of their spectral data and chemical reactions, i.e., The IR spectrum of (7b) showed an amide carbonyl bond at 1640 cm^{-1}. Catalytic hydrogenation of (7a) over paladium-charcoal gave N-methylphthalimidine(8; mp 115°) in 50% yield, which can be formed *via* reductive cleavage of the diaziridine ring, accompanied by loss of ammonia, and subsequent cyclization.6) Treatment of (7a and b) with trifluoroacetic acid caused the smooth conversion into (6).

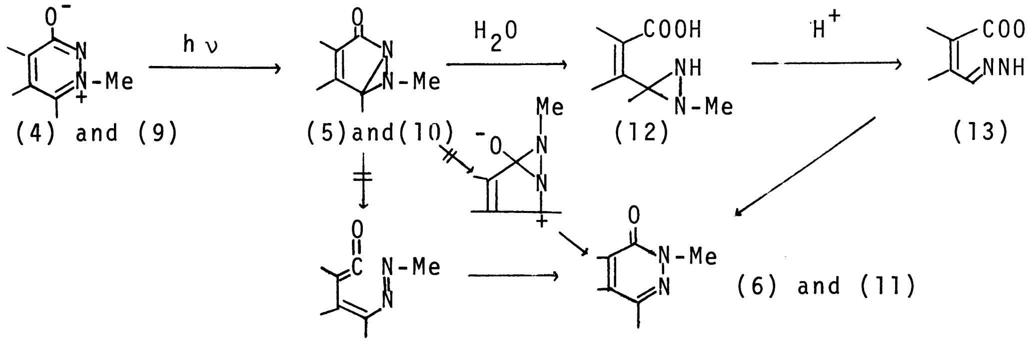
The fused diaziridine(5) was transformed with ease into (6) when it was allowed to stand in acetonitrile containing water at room temperature in the dark. This conversion was significantly accelerated by addition of trifluoroacetic acid.

Analogously, the irradiation of pyridazine betaine(9) in acetonitrile gave the fused diaziridine(10) as an oil [IR spectrum(KBr, cm^{-1}) 1745 C=O; NMR spectrum ($CDCl_3$, δ) 1.72 CCH_3, 2.68 NCH_3, 5.78 and 7.57 an AB-type quartet J= 5.5 Hz vinyl protons; mass spectrum m/e M^+= 124]. Conversion of (10) into 2,6-dimethyl-3(2H)-pyridazinone (11) was observed upon treatment with water at room temperature.

The fused diaziridines(5) and (10) are presumably formed from betaines(4) and (9) by a photochemically allowed disrotatory ring closure. Although various fused diaziridines have beeb proposed as intermediates in the photoisomerization of some heterocyclic compounds7), only 6-phenyl-1,5-diazabicyclo[3:1:0]hexane has been isolated upon irradiation of 1-benzylidene-3-oxidopyrazolidinium betaine.8)

As mentioned above, the amide bond of (5) and (10) is sensitive to aminolysis and alcoholysis. Such facility of the amide bond could be explained in terms of the less amide resonance resulting from the inefficient overlapping between the p-orbital of the bridgehead nitrogen and the π-orbital of the carbonyl group in (5) and (10). (see A in Scheme 2) The high frequency amide carbonyl band observed in their IR spectra is parallel to this explanation.

The isomerization of (5) and (10), consequently (4) and (9), to (6) and (11)



Scheme 3

in water could involve an intermediacy of carboxylic acid (12) produced by hydrolysis of the weak amide bond. The carboxylic acid intermediate (12) undergoes the diaziridine ring cleavage due to the protonation by a carboxylic proton. The hydrazone (13) thus formed can be cyclized spontaneously to (6) and (11). Acceleration of the conversion of (5) and (10) to (6) and (11) by addition of acids is relevant to the above process. The inefficient conversion of (9) into (11) by the irradiation in water may be ascribed to the thermal or photochemical instability of the intermediate (10) in comparison with (5).[9]

Previously, we proposed that the photoisomerization of (1) to (3) could proceed *via* the fused diaziridine intermediate (2) which subsequently gives a ketene intermediate or a zwitterionic intermediate. The present study, however, clearly demonstrated no occurrence of such a type of photoisomerization in the betaines (4) and (9) employed in the present study. (see Scheme 3)

References and Footnotes

1) This paper forms photochemical Reactions Part XVIII. Part XVII : *J. Amer.Chem. Soc.*, **99** (1977) in press.
2) Y. Maki, M. Suzuki, T. Furuta, T. Hiramitsu, and M. Kuzuya, *Tetrahedron Letters*, **1974**, 4109.
3) D. E. Ames, S. Chandraskhar, and R. Simpson, *J. Chem. Soc. Perkin I*, **1975**, 2035.
4) N. Dennis, A. R. Katritzky, and M. Ramaiah, *J. Chem. Soc. Perkin I*, **1976**, 1509.
5) All new compounds exhibited satisfactory NMR, IR and mass spectra as well as combustion analyses(C,H ± 0.4%).
6) Reductive cleavage of diaziridines accompanied with loss of amines has been well documented (e.g. E. Schmitz and D. Habisch, *Chem. Ber.*, **95**, 680 (1962)).
7) For example, J. M. Cassel and J. Streith, *Tetrahedron Letters*, **1976**, 4859.
8) M. Schultz, G. West, U. Muller, and D. Henke, *J. Prakt. Chem.*, **318**, 946 (1976).
9) More recently, 6-phenyl-6-azabicyclo[3:1:0]hex-3-ene-2-one, deazaanalog of our fused diaziridine system, has been obtained in the crystalline form by irradiation of 3-oxido-1-phenylpyridinium. It has been elucidated that the bicyclic intermediate undergoes further thermal and photochemical reactions (N. Dennis, A. R. Katritzky, and H. Wilde, *J. Chem. Soc. Perkin I*, **1976**, 2338).

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