

Oxidative Ring Contraction of the  
1,2-Dihydro-1,3-dimethyl-2-oxopyrimidinium Cation to  
3-Methyl-2,4-oxazolidindione

*Oswald S. Tee\* and Masaki Endo*

Department of Chemistry, Sir George Williams Campus, Concordia University  
Montreal, Quebec H3G 1M8 Canada

Received June 23, 1975

Quaternary heteroaromatic cations are often oxidizable to oxo derivatives, presumably *via* their pseudo-bases (I). For example, the 1-methyl-pyridinium ion in alkaline potassium ferricyanide solution yields 1-methyl-2-pyridinone in good yield (2). By analogy, one would expect the 1,2-dihydro-1,3-dimethyl-2-oxopyrimidinium cation (I), which exists in aqueous solution in equilibrium with its pseudo-base (II) (3), to be oxidizable to 1,3-dimethyluracil (III). Such a reaction might provide a fairly general route to 1,3-disubstituted uracils since a variety of 1,3-disubstituted cations related to I can be made in good yields from the direct cyclization of readily available ureas and malondialdehyde (4).

Attempted oxidations of the 1,3-dimethyl cation (I; anion =  $\text{HSO}_4^-$ ) (5) using alkaline potassium ferricyanide gave only small quantities of unidentified oils, and no isolable amounts of III. Since hydrogen peroxide/acetic acid has been used in a related oxidation of quinazoline to 4-quinazolinone (6), these reagents were also tried.

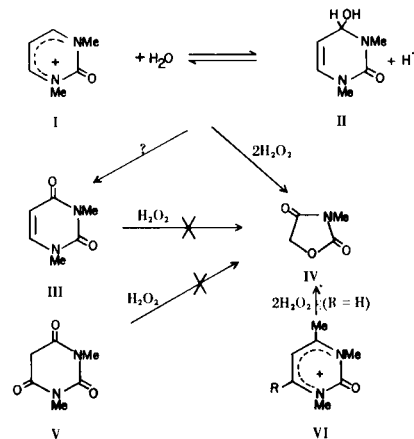
The reaction of I (as bisulfate) with 2.3 equivalents of hydrogen peroxide in acetic acid at 60-65° for 2 hours did not give the expected III, but produced 3-methyl-2,4-oxazolidindione (IV) in good yield. The identification of IV followed from its elemental analysis, its ir, pmr, and also from comparison with a sample of IV made by the reaction of ethyl *N*-methylcarbamate and chloroacetyl chloride (7). IV was also obtained from oxidations using 2.3 equivalents of hydrogen peroxide in water or in basic solution (pH ~ 9). However, if only 1.15 equivalents of hydrogen peroxide were used *no* product was obtained, even when the reaction time was extended from 2 to 21 hours (see Table).

The oxazolidindione (IV) is not derived from further oxidation of the expected 1,3-dimethyluracil (III), since the latter was unaffected by hydrogen peroxide in acetic acid under the same reaction conditions. Similarly, another potential oxidation intermediate, 1,3-dimethylbarbituric acid (V) did not give IV when submitted to oxidation.

In addition to IV, the oxidation of I appears also to produce formic acid, which was observable in pmr spectra

of reaction mixtures. Moreover, oxidation of the trimethyl cation VI (R = H) in water also gave IV, and pmr spectra of the product mixture showed the presence of acetic acid. On the other hand, the tetramethyl cation IV (R = Me) does not undergo oxidation under the same conditions.

For the present, the mechanism of these interesting reactions remains obscure, although they may well involve pseudo-bases (or similar intermediates) since the latter are very susceptible to electrophilic attack (5). Other oxidative ring contractions which may provide clues are the peroxide induced conversion of pyrylium cations to furans (8), and, in particular, the contraction of barbituric acid derivatives to oxazolidindiones (9). It has also been reported that



3-carbamoylpyridinium salts with hydrogen peroxide produce pyrrolidinone hydroperoxides, but in poor yields (10). A future study will be directed towards elucidation of the mechanism of the present reactions.

#### EXPERIMENTAL

The pyrimidinium salts (I, VI, bisulfates) were made as described previously (4,5). 1,3-Dimethyluracil was a commercial sample, while 1,3-dimethylbarbituric acid was prepared by a literature method (11). Elemental analyses were performed by Galbraith Labs., Inc., Knoxville, Tenn.

Table  
Oxidation Experiments

Substrate	30% Hydrogen peroxide (Equivalent)	Solvent	Temperature (°C)	Time (hours)	Yield IV %	Remarks
I, HSO <sub>4</sub> <sup>-</sup>	2.3	Acetic acid	60-65	2	70	
	2.3	Acetic acid	60-65	1	44	
	1.15	Acetic acid	60-65	2	0	Recovered substrate
	1.15	Acetic acid	60-65	21	0	Recovered substrate
	2.3	Water	70-75	6	61	
	2.3	Water	room	96	100	
	2.3	Water, pH 9	60-65	3	52	
III	2.3	Acetic	60-65	2	0	Recovered substrate
V	2.3	Acetic acid	65-70	2.5	0	Unidentified product
VI (R = H), HSO <sub>4</sub> <sup>-</sup>	2.3	Water	70-75	6	43	
VI (R = Me), HSO <sub>4</sub> <sup>-</sup>	2.3	Water	70-75	6	0	Recovered substrate

Oxidation of 1,2-Dihydro-1,3-dimethyl-2-oxopyrimidinium Bisulfate.

To a solution of the salt (0.01 mole) in 20 ml. of acetic acid was added 2 ml. of 30% hydrogen peroxide (0.023 mole). The mixture was warmed at 60-65° for 2 hours. Removal of the solvent under reduced pressure gave a slurry of crystals. To this was added 10 ml. of water to facilitate azeotropic removal of the remaining acetic acid under reduced pressure. This left 0.8 g. (70%) of crystals of IV. Purification of IV was either by recrystallization from ligroin-ethanol, or by sublimation, m.p. 133-134°.

*Anal.* Calcd. for C<sub>4</sub>H<sub>5</sub>NO<sub>3</sub>: C, 41.75; H, 4.38; N, 12.16. Found: C, 41.80; H, 4.42; N, 12.30.

The material obtained as described above had exactly the same ir, pmr, mass spectral properties as 3-methyl-2,4-oxazolidindione made by a literature procedure (7).

All oxidations, which were carried out in a similar manner to that above, are summarized in the Table.

Acknowledgments.

The authors thank the National Research Council of Canada for financial support, and Dr. T. J. Adley for kindly running the mass spectra.

#### REFERENCES AND NOTES

- (1) H. Decker, *Chem. Ber.*, **25**, 443 (1892); H. Decker, *J. Prakt. Chem.*, **47**, 28 (1893); A. Hantzsch, *Chem. Ber.*, **32**, 575 (1899); A. Hantzsch and M. Kalb, *ibid.*, **32**, 3109 (1899); J. W. Bunting and W. G. Meathrel, *Can. J. Chem.*, **48**, 3449 (1970).
- (2) E. A. Prill and S. M. McElvain, *Organic Synthesis*, Coll. Vol. 2, 419 (1943).
- (3) A. R. Katritzky, M. Kingsland and O. S. Tee, *J. Chem. Soc.*, (B), 1484 (1968).
- (4) O. S. Tee and M. Endo, *J. Heterocyclic Chem.*, **11**, 441 (1974).
- (5) O. S. Tee and S. Banerjee, *Can. J. Chem.*, **52**, 451 (1972).
- (6) A. Albert, W. L. F. Armarego and E. Spinner, *J. Chem. Soc.*, 2689 (1961).
- (7) M. Pinanka and D. J. Polton, *ibid.*, 983 (1960).
- (8) A. T. Balaban, *Org. Prep. Proced.*, **1**, 63 (1969).
- (9) H. C. Van der Plas, "Ring Transformations of Heterocycles", Vol. 2, Academic Press, N. Y., 1973, pages 125 *et seq.*
- (10) D. W. Bristol and D. C. Dittmer, *J. Org. Chem.*, **35**, 2487 (1970).
- (11) J. W. Clark-Lewis and M. J. Thompson, *J. Chem. Soc.*, 1628 (1959).