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Oxidation of 1,2-dihydro-1,3-dimethyl-2-oxopyrimidinium bisulfate ($1^+.HSO_4^-$) with hydrogen peroxide in acetic acid in the presence of potassium iodide gave 1,3-dimethyl-5-iodouracil (65-70%), 1,3-dimethyluracil (10-15%) and 3-methyl-2,4-oxazolidinedione (10-15%). Similar results were obtained on oxidation of the iodide ($1^+.I^-$). Oxidation of 1-methyl-4-phenylpyrimidinium iodide or oxidation of 1-methyl-4-phenylpyrimidinium methylsulfate in the presence of potassium iodide gave 1,6-dihydro-5-iodo-1-methyl-6-oxo-4-phenylpyrimidine.

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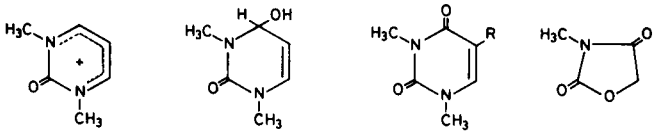
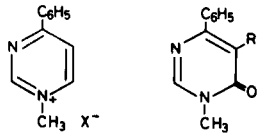
1,2-Dihydro-1,3-dimethyl-2-oxopyrimidinium ions are in equilibrium with their pseudo-bases (1,2). Attempts to prepare 1,3-dimethyluracil (**3**) by oxidation of the 1,3-dimethyl-2-oxopyrimidinium bisulfate ($1^+.HSO_4^-$), the cation 1^+ is in equilibrium with **2**, using hydrogen peroxide in acetic acid, failed; the ring contraction product 3-methyl-2,4-oxazolidinedione (**5**) and not the expected product 1,3-dimethyluracil (**3**) was isolated (3). When, however, instead of the bisulfate salt ($1^+.HSO_4^-$) the iodide salt ($1^+.I^-$) was treated with hydrogen peroxide in acetic acid a completely different reaction took place. Only a small amount of **5** was formed and as main product a mixture of **3** and its 5-iodo compound **4** was obtained in nearly quantitative yield. Compound **4** is found to be formed from **3** by iodination with the iodine, which is liberated during the treatment of $1^+.X^-$ with the hydrogen



1' **2** **3** (R=H) **4** (R=I) **5**

peroxide. The success of this oxidation procedure induced us to reinvestigate the oxidation of $1^+.HSO_4^-$ with hydrogen peroxide in acetic acid, now, however, in the presence of *potassium iodide*. We observed that under these conditions both products **3** and **4**, together with only small amounts of **5**, were obtained. Apparently the oxidation of the secondary hydroxyl group in the pseudo-base **2** into the 4-oxo group easily took place and the presence of the iodine prevented further oxidation of the greater part of **3** into **5**. Possibly adduct formation between **3** and iodine and conversion of **3** into the 5-iodo compound **4** prohibited the subsequent oxidation.

Nearly analogous results were obtained with 1-methyl-4-phenylpyrimidinium iodide (**6**) ($X^- = I^-$). Treatment of **6** ($X^- = I^-$) with hydrogen peroxide in acetic acid at 70° led to oxidation at position 6 and iodination at position 5, yielding 1,6-dihydro-5-iodo-1-methyl-6-oxo-4-phenylpyrimidine (**8**); as by-products benzoic acid and benzamide were formed in small amounts. The 6-oxo compound **7** can be considered to be the precursor of **8**. When the



6 **7** (R=H) **8** (R=I)

oxidation of **6** ($X^- = I^-$) was carried out at *room* temperature, **7** was nearly the sole product; only a trace of **8** was formed. Furthermore it was found that treatment of **7** with hydrogen peroxide in acetic acid containing potassium iodide at about 70° effectively iodinated **7** into **8**. As expected, oxidation of the salt (**6**, $X^- = CH_3SO_4^-$) in the presence of potassium iodide also gave compound **8**.

Attempts to oxidize 1,2-dihydro-1-methyl-2-oxo-4-phenylpyrimidine with hydrogen peroxide in acetic acid containing potassium iodide were unsuccessful. Besides a small amount of 5-iodo-1-methyl-4-phenyluracil, many decomposition products derived from benzoic acid were found.

EXPERIMENTAL

The pyrimidinium salts $1^+.HSO_4^-$ (4,5), $1^+.I^-$ (4,5), 1-methyl-4-phenylpyrimidinium iodide (**6**, $X^- = I^-$) (6), 1,6-dihydro-6-oxo-4-phenylpyrimidine (**7**) (7) and 1-methyl-4-phenylpyrimidinium methylsulfate (**6**, $X^- = CH_3SO_4^-$) (8) were prepared as described previously.

1. Oxidation of 1,2-Dihydro-1,3-dimethyl-2-oxopyrimidinium Iodide ($1^+.I^-$).

A solution of 0.76 g. of $1^+.I^-$ (0.003 mole) in 6 ml. of acetic acid was heated with 0.6 ml. of hydrogen peroxide (30%) at 60-65° for two hours. After evaporation of the solvent, a residue was obtained which was taken up in chloroform. After washing with aqueous sodium bisulfite and subsequently with water, the chloroform was dried over magnesium sulfate. Evaporation of the solvent gave 0.57 g. of a residue, from which by column chromatography on silica gel, using chloroform as eluent, the following compounds could be isolated:

1,3-Dimethyl-5-iodouracil.

This compound was obtained in a yield of 0.17 g. (20-25%), m.p. 235-236° (lit. (9,10) 124-125°); exact molecular weight (by mass spectrometry) 265.9564; Calcd. 265.9554; nmr (DMSO-d_6): δ 3.22 ppm (3H, s, NCH_3), 3.31 ppm (3H, s, NCH_3), 8.22 ppm (1H, s, H-6).

1,3-Dimethyluracil.

This compound was obtained in a yield of 0.3 g. (70-75%), m.p. 123-124° (lit. (11) 123-124°) molecular weight (by mass spectrometry) 140; nmr (acetone-d_6): δ 3.20 ppm (3H, s, NCH_3), 3.37 ppm (3H, s, NCH_3), 5.55 ppm (1H, d, H-5), 7.50 ppm (1H, s, H-6), $J_{5,6}$ = 8 Hz.

2. Oxidation of 1,2-Dihydro-1,3-dimethyl-2-oxopyrimidinium Bisulfate (**1**$^+$.HSO_4^-) in the Presence of Potassium Iodide.

A solution of 2.0 g. of **1**$^+$.HSO_4^- (0.009 mole) in 20 ml. of acetic acid, containing 1.66 g. of potassium iodide was heated with 2 ml. of hydrogen peroxide (30%, hydrogen peroxide) at 65-70° for two hours. The work-up was performed as described in section 1. After evaporation of the chloroform 2.08 g. of a residue were obtained from which by addition of a small amount of absolute methanol 1.58 g. of 1,3-dimethyl-5-iodouracil separated (yield 65-70%, m.p. 235-236°, nmr and mass spectrum identical with that of an authentic specimen (9). The mother liquid contained, as shown by nmr spectroscopy and mass spectrum, 3-methyl-2,4-oxazolidinedione (10-15%) and 1,3-dimethyluracil (10-15%).

3. Oxidation of 1-Methyl-4-phenylpyrimidinium Iodide (**6**, X^- = I^-).

Compound **6** (2.98 g., 0.01 mole) (X^- = I^-) was dissolved in 30 ml. of acetic acid and heated with 7.5 ml. of hydrogen peroxide (30%) at 70° for seven hours. After diluting with 50 ml. of water, 1.1 g. of 1,6-dihydro-5-iodo-1-methyl-6-oxo-4-phenylpyrimidine (**8**) was isolated. By extraction of the solution an additional amount of **8** (0.40 g.) was obtained. Total yield of **8** was 1.55 g. (40-45%), m.p. 170-171° (from benzene-petroleum ether (b.r. 60-80°)); exact molecular weight (by mass spectrometry) 311.9760; Calcd. 311.9762; nmr (acetone-d_6): δ 8.38 ppm (1H, s, H-2); 7.6 ppm (5H, m, C_6H_5), 3.61 ppm (3H, s, NCH_3).

Anal. Calcd. for $C_{11}H_9IN_2O$: C, 42.33; H, 2.91. Found: C, 42.25; H, 2.86.

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