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N-VINYLATION OF HETEROAROMATIC O-TRIMETHYLSILYL LACTIMS*

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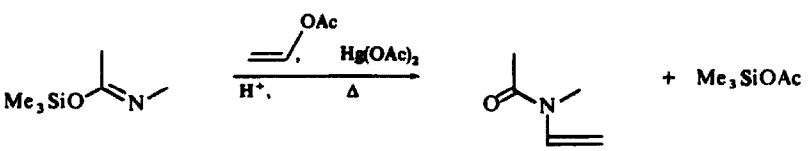
Abstract—By combining the Hilbert-Johnson and vinylester interchange reactions, a new hybrid reaction has been developed for the convenient synthesis of N-vinylpyrimidinone and N-vinylpyridone monomers. The appropriate O-trimethylsilyl heteroaromatic lactims when heated with vinyl acetate and catalytic amounts of both mercuric acetate and sulfuric acid afforded 1-vinyluracil, 1-vinyl-2-pyridone, 1-vinyl-4-pyridone, and N-acetyl-1-vinylcytosine respectively. The relative reactivity was found to decrease with the estimated decrease in the pKa's of the heteroaromatic lactims. 2-Ethoxypyridine did not react. The mechanism of the reaction is discussed.

IN THE course of our investigation[1,2] of simple vinyl polymers, which are nucleic acid analogs, we have been interested in developing a simple, general synthesis of N-vinylpyrimidinones. The simplest pyridmidine nucleic acid analog monomer, 1-vinyluracil (I), has been synthesized by dehydrohalogenation of 1-(2-chloroethyl)-uracil[1,3,24] and by cyclization of N-β-ethoxy acryl-N-vinyl urea.[1] These procedures suffer from either too many steps or low yields in obtaining the needed intermediates.

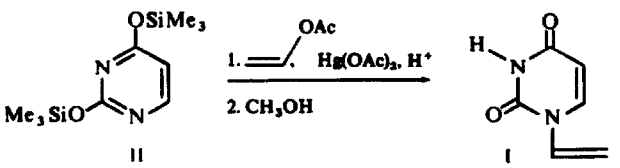
With knowledge of the mechanisms of the Hilbert–Johnson[4,5] and vinylester interchange reactions,[6,7] it seemed feasible that if we combined these reactions and incorporated trimethylsilyl groups, a new hybrid reaction for the convenient synthesis of the desired monomers would be developed. It is our purpose here to report



on the success and general scope of this new reaction.

RESULTS

The reaction of 2,4-bis (trimethylsilyl) uracil (II)[8] with refluxing vinyl acetate and catalytic amounts of both sulfuric acid and mercuric acetate afforded 1-vinyluracil (I) after five days in an anhydrous atmosphere.



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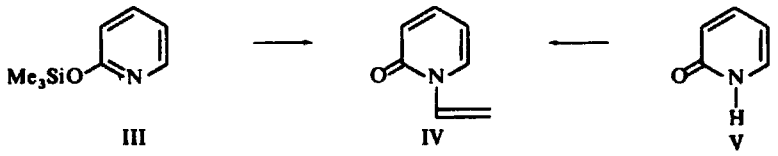
The product was identical with I which was prepared by our earlier procedures.[1] Trimethylsilyl acetate was detected in the reaction mixture by GLC.

In order to obtain some information about the generality of this new N-vinylation procedure, the reaction of 2-trimethylsilyloxypyridine (III)[9] was investigated. After carrying out the reaction for 36 hr TLC indicated quantitative conversion to 1-vinyl-2-pyridone (IV).

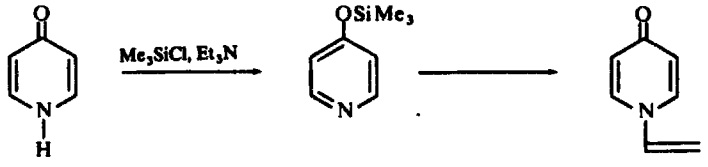


III IV V

The structure of IV was confirmed by IR[10], NMR[11] (Table I), and the fact that the picrate melted at the literature value.[12]

It was of interest to compare our new procedure with the direct N-vinylation of 2-pyridone (V) by the vinylester interchange method. This reaction proceeded in only about 50% conversion (TLC) to IV after five days of heating at reflux.

Trimethylsilylation of 4-pyridone (VII) was carried out by the general procedure of Birkofer[9] to yield VI. The structure of this compound was confirmed by the presence

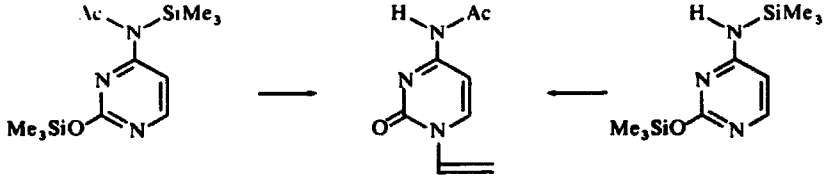


VII VI VIII

of IR bands for a 4-substituted pyridine[10] and the absence of CO absorption in the 1650 cm^{-1} vicinity. Vinylation of VI under the usual conditions gave quantitative conversion to 1-vinyl-4-pyridone (VIII) as detected by TLC after 36 hr. The IR[10] and NMR (Table I) spectra were consistent with the structure for VIII.

With the success of the above reactions, it seemed worthwhile to test the behavior of 2-ethoxypyridine as it is well known that this compound can undergo the Hilbert–Johnson reaction.[13] In contrast to the results obtained above, no reaction could be detected after one week of heating at reflux.

The reaction of 2,4-bis (trimethylsilyl)-N^4-acetylcytosine[14] (IX) was also not successful under the usual conditions, however, under forcing conditions in a sealed tube, conversion to N-acetyl-1-vinylcytosine (X) was achieved. Vinylation of 2,4-bis (tri-

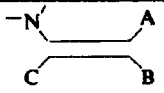


IX X XI

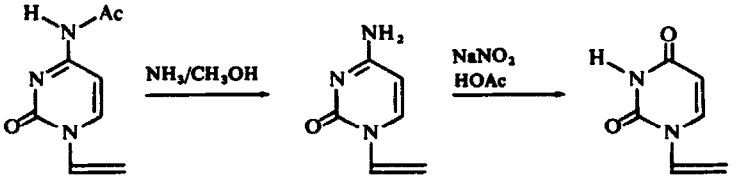
methylsilyl) cytosine[14] (XI) proceeded under normal conditions to X and lesser amounts of two unidentified products after two days of reaction. This result is quite novel because the vinyl acetate has selectively behaved as both a vinylating and acetylating agent. Unequivocal proof of structure for X was obtained by NMR (Table 1) and by conversion to 1-vinylcytosine (XII) with methanolic ammonia followed by deamination of XII with nitrous acid to I.

TABLE 1. NUCLEAR MAGNETIC RESONANCE PARAMETERS OF N-VINYL MONOMERS

	δ Chemical Shift Values of Protons*							
Compound	A	B	C	2	3	4	5	6
I[a]	5·38q	4·91q	7·13q	—	11·44s	—	5·76d	8·02d
	J_{AB} = 1·8	J_{BC} = 8·4	J_{AC} = 16·0				J_{56} = 8·0	
X[a,c]	5·93q	5·48q	7·64q	—	—	11·36s	7·64d	8·70d
	J_{AB} = 1·8	J_{BC} = 9·0	J_{AC} = 16·0				J_{56} = 7·4	
XII[a]	5·58q	5·14q	7·61q	—	—	7·74s	6·20d	8·25d
	J_{AB} = 1·8	J_{BC} = 9·0	J_{AC} = 16·0				J_{56} = 7·4	
IV[b]	5·30q	5·01q	7·56q	—	6·51d	7·53(m)	6·19t	7·26q
	J_{AB} = 1·50	J_{BC} = 9·0	J_{AC} = 16·2		J_{34} = 9·4		J_{45} = J_{56} = 6·4	J_{46} = 2·0
VIII[b]	5·28q	4·95q	6·81q	7·70d	6·38d	—	—	—
	J_{AB} = 2·8	J_{BC} = 8·8	J_{AC} = 15·8	J_{23} = 7·8				



* N Acetyl protons = 2·50 S.
s = singlet, d = doublet, t = triplet, q = quartet.
[a] Measured in DMSO (d_6) with an external standard
[b] Measured in $DCCl_3$ with an internal standard.
Coupling constants are reported in H_Z.



X XII I

The UV absorption spectra of the N-vinyl compounds reported in this paper deserve some comment. In Table 2 are listed the λ_{max} values of the N-vinyl compounds

and their corresponding 1-saturated derivatives. The λ_{max} values of the N-vinyl compounds are bathachromically shifted 12 to 23 mμ from the normal values reported for these ring systems even though the vinyl groups are not directly conjugated with the double bonds in the rings. This effect demonstrates that the aromatic resonance forms for these ring systems are important.

TABLE 2. UV DATA*

N-Vinyl compound	λ_{max} mμ	λ_{max} of Sat. Cmpd. mμ	Difference mμ
I	277	265[15]	12
X	312	297	15
XII	286	271[15]	15
IV	311	297[16]	14
VIII	283	260[16]	23

* Comparisons were made at the same pH values.

DISCUSSION

The N-vinylation mechanism (Chart I) that seems consistent with the experimental results is based on the suggested mechanisms of the Hilbert–Johnson[4] and vinyl ester interchange[6] reactions, both of which have convincing evidence. The formation of an intermediate such as XIV is supported by the fact that a similar intermediate has been isolated in the Hilbert–Johnson reaction.[5] Dreiding models of III indicate that the 2-trimethylsilyloxy group must be anti to the 1-nitrogen for attack to take place by the mercurinum ion XIII. The faster reactions of III and VI compared to the pyrimidine derivatives II and IX are consistent with the greater bascity of the pyridines leading to greater stability of the XIV type intermediates. Although the pKa values of the trimethylsilyoxy derivatives are unknown we can obtain a rough relative comparison of basicity from the p*Ka*'s of the corresponding methoxy derivatives. The p*Ka* values of 4-methoxypyridine and 2-methoxypyridine are 6·62 and 3·28, respectively.[17] We estimate that 2,4-bis(trimethyl)uracil may have a p*Ka* around 2·4* in support of the slower reaction of II.

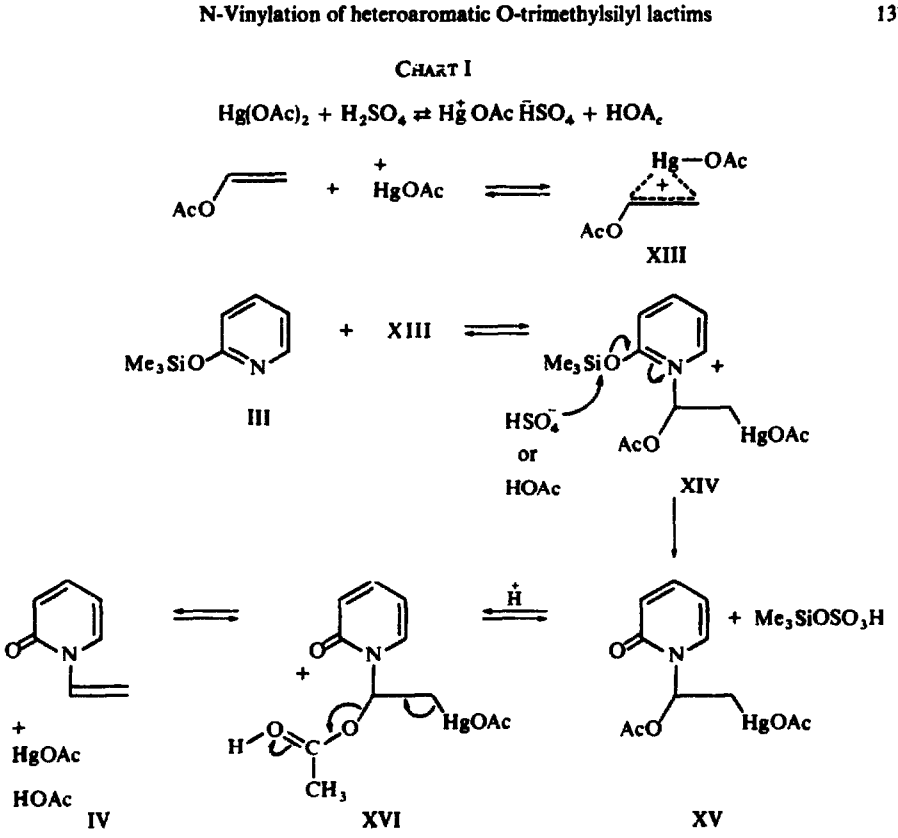
Our estimated p*Ka* value of 0·7† for 2,4-bis(trimethyl-N⁴-acetylcytosine is also consistent with the fact that IX reacts only under driving conditions. A molecular model of IX indicates that the necessary anti conformation of the 2-trimethylsilyl group is sterically hindered by either the N-acetyl or N-trimethylsilyl group and this may be an additional factor contributing to the low reactivity. This mutual repulsion is expected to enhance the steric hinderance of resonance for the trimethylsilylamino group.

Removal of the N-acetyl group from IX eliminates the above effects and the 4-trimethylsilylamino group can then donate electron density to the ring by resonance making XI more basic than IX. We estimate that the p*Ka* of 2,4-bis(trimethyl)cytosine

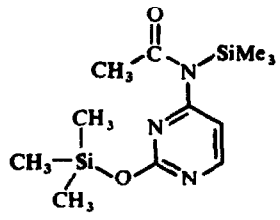
* From reference 17. 2-methoxy-4-methylpyrimidine *pKa* = 2·10, pyrimidine *pKa* = 1·30, 4-methoxypyridine *pKa* = 2·50, 4-methylpyridine *pKa* = 6·02 and pyridine *pKa* = 5·17. ∴ 2·10 − (6·02 − 5·17) + (2·5 − 1·31) = 1·25 + 1·19 = 2·4.

† 4-(Acetyl-N-methylamino)pyridine *pKa* = 4·62, pyridine *pKa* = 5·17. ∴ 1·25 − (5·17–4·62) = 1·25 − 0·55 = 0·7.

CHART I



$$Me_3SiOSO_3H + HOAc \rightleftarrows Me_3SiOA_c + H_2SO_4$$



IX

may be around 6·1* and this is consistent with the relatively rapid reaction of XI. The precise mechanism by which the acetyl is introduced onto the 4 amino group of XI during vinylation is not yet clear, although it is reported that vinyl acetate can acetylate

* 4-methylaminopyrimidine $pKa = 6{\cdot}12$, pyrimidine $pKa = 1{\cdot}30$ and 2-methoxyprimidine as estimated above $pKa = 1{\cdot}25$.

$\therefore 1{\cdot}25 + (6{\cdot}12 - 1{\cdot}30) = 1{\cdot}25 + 4{\cdot}82 = 6{\cdot}1$.

imidazole.[18] To know whether the N—Si[19] or N—H bond is cleaved during the reaction will require further work. In any event, IX is certainly not formed as an intermediate, otherwise the vinylation would not have proceeded so readily.

The collapse of intermediate XIV is expected to take place by attack of the bisulfate ion and/or acetic acid on the trimethylsilyl group. This is supported by the well known fact that trimethylsilyl groups are readily attacked by weak nucleophiles[19] and by our experimental observation that 2-ethoxypyridine does not react, most probably, because the C—O bond cannot be broken by such weak nucleophiles.

The remainder of steps (XV–IV) is directly analogous to the vinyl ester interchange mechanism.[6] Conversion of XVI to IV may also proceed stepwise through a mercurinium ion. Although formation of trimethylsilyl hydrogen sulfate[20] has not been demonstrated, it seems possible that if it is formed, it may trimethylsilylate acetic acid in analogy with the reaction of acetic acid and isopropyl hydrogen sulfate.[21] The possibility of more complicated trimethylsilyl exchange reactions cannot be ruled out at this time however.[22,23]

The alternative possibility of a concerted cyclic mechanism for the vinylation reaction is thought not to be probable because molecular models indicate too much crowding in the transition state and also because VI, a compound which cannot undergo a cyclic reaction, can be N-vinylated readily.

EXPERIMENTAL

All m.ps are corrected and analyses were carried out by Alfred Bernhardt Mikroanalytisches Laboratorium, Elbach Über Engelskirchen, Germany. UV spectra were measured with a Cary 14. IR spectra were measured with a Beckman IR-8 and a Perkin Elmer 541. Barns Engineering NaCl cells were used for the IR analyses of the moisture sensitive trimethylsilyloxy pyridines. NMR spectra were determined at 33° on a Varian HA 100 m.c. instrument operating in the frequency mode locked on TMS. TLC was carried out on microscope slides coated with Merck 254 G silicic acid. Chromatograms were developed with MeOH-$CHCl_3$ mixtures and spots were detected with a short wavelength UV lamp. GLC was carried out on an F & M 5750 flame ionization instrument.

1-Vinyluracil (I)

2,4-Bis(trimethylsilyl)uracil[8] (54 g, 0·21 mole) was refluxed with dry vinyl acetate (200 ml), mercuric acetate (200 ml), mercuric acetate (3·3 g), and conc H_2SO_4 (0·7 ml) under a slight positive pressure of dry N_2. For every day of the reaction 0·5 g diphenylamine (recrystallized) was added as a polymerization inhibitor. After 5 days nearly complete conversion to the vinylated product was indicated by TLC. The solvent was removed with care to avoid moisture. GLC of the distillate on a 6 ft UCW98 silicon capillary column at 70° indicated a peak with the same retention time as an authentic sample of trimethylsilyl acetate. This peak disappeared when the mixture was hydrolyzed with MeOH. The residue was placed under high vacuum to remove all traces of solvent and then MeOH (400 ml) was added followed by enough conc NH_4OH to neutralize any acid present. The mixture was reduced to dryness and the residue was extracted with four 1 liter portions of boiling toluene. A total of 8·7 g (30%) of white needles was obtained. After recrystallization from water, the 1-vinyluracil melted at 180–180·5: UV max (0·1 NaOH) 277 mμ (ε 9987), 222 mμ (ε 11,782), shoulder at 233 mμ; IR (nujol) 3160 (w), 3020 (m), 1740 (s), 1675 (s), 1630 (s), 1620 (s), 1410 (m), 1330 (m), 1278 (m), 1210 (s), 1100 (w), 970 (w), 860 (m), 827 (s), 790 (w), 758 (m), 752 (m) and 727 cm^{-1} (m); the product was identical with authentic[1] 1-vinyluracil by mixture m.p., IR spectroscopy and TLC.

1-Vinyl-2-pyridone (IV)

(a) 2-Trimethylsilyloxypyridine[9] (5 g, 0·0295 mole) was refluxed with dry vinyl acetate (25 ml), mercuric acetate (0·2 g), and H_2SO_4 (40 μl) for 36 hr under a N_2 atmosphere. TLC indicated quantitative conversion to product. After removing all solvent, ether (25 ml) and anhyd NaOAc (2 g) were added. The mixture was filtered and the ether removed. Distillation of the residue through a short path distillation apparatus afforded 1-vinyl-2-pyridone (2·72 g, 75%) as a faintly, yellow-tinted oil: b.p. 103°/1·6 mm; m.p. 23–25°;

picrate m.p. 89–91°, [b.p. 251°/750 mm picrate m.p. 91–92·5].[12] Found: C, 69·20; H, 5·90; N, 11·50. Calcd. for C_7H_7NO: C, 69·41; H, 5·82; N, 11·55%); UV max (H_2O) 311 mμ (ε 4194), 212 mμ (ε 6755); IR (melt) 3060 (m), 1650 (s), 1575 (s), 1527 (s), 1445 (w), 1400 (vw), 1375 (m), 1320 (m), 1260 (m), 1220 (w), 1190 (m), 1140 (m), 1100 (w), 965 (m), 892 (m), 865 (m), 840 (m), 763 (m), 742 (m) and 675 cm^{-1} (w).

In the liquid state IV is extremely hygroscopic, and on standing at room temp for a day it discolors to light purple. In a later preparation, TLC indicated quantitative conversion to product after 7 hr of reflux.

(b) 2-Pyridone (10 g, 0·105 mole) was refluxed with vinyl acetate (100 ml), mercuric acetate (0·4 g), and H_2SO_4-H_2O (1:1) (0·1 ml) for 5 days. At that time TLC indicated only partial conversion to product. The mixture was reduced to dryness and ether (200 ml) was added. The organic phase was extracted with 10% NaOH (25 ml), dried (Na_2SO_4), concentrated, and distilled through a short path distillation apparatus yielding 1-vinyl-2-pyridone (1·82 g, 14·3%): b.p. 106°/1·3 mm; m.p. 23–25°; the product was identical to the material prepared in Part A by TLC and IR spectroscopy.

4-*Trimethylsilyloxypyridine* (VI)

The procedure of Birkofer[9] for the preparation of III was used. 4-Pyridone (50 g, 0·526 mole) and trimethylsilylchloride (52 g, 0·48 mole) were refluxed with Et_3N (100 ml) and toluene (250 ml) for 9 hr under anhydrous conditions. The mixture was filtered on a fritted glass filter and the filtrate was reduced to an oil under reduced press with care to avoid moisture. Distillation through a 10 in vigreux column afforded 4-trimethylsilyloxypyridine (40·6 g, 46·3%), b.p. 81°/5 mm, as a colorless oil. (Found: C, 57·25; H, 7·90; N, 8·09. Calcd. for $C_8H_{13}ONSi$: C, 57·44; H, 7·83; N, 8·37%); IR (CCl_4) 3025 (w), 2980 (s), 1585 (s), 1560 (m), 1490 (m), 1415 (w), 1385 (w), 1288 (s), 1255 (s), 1205 (m), 1090 (w), 1050 (w), 993 (m), 920 (s), 847 (s) and 735 cm^{-1} (s). The compound hydrolyses very rapidly on exposure to air.

1-*Vinyl-4-pyridone* (VIII)

4-Trimethylsilyloxypyridine (11 g, 0·066 mole) was refluxed with dry vinyl acetate (50 ml), mercuric acetate (0·4 g), and H_2SO_4 (80 μl) for 36 hr under N_2. TLC indicated quantitative conversion to product. After removal of solvent, $CHCl_3$ (50 ml) was added and the mixture was extracted with 0·3 N NaOH (3 ml) and then dried (Na_2SO_4). Removal of the $CHCl_3$ followed by distillation through a short path distillation apparatus yielded 1-vinyl-4-pyridone (3·0 g, 37·6%) as a colorless oil which crystallized in the receiver: b.p. 147–148°/0·25 mm; m.p. 82–87°; picrate (ETOH) m.p. 200–202°; hygroscopic. (Found: C, 69·27; H, 5·96; N, 11·70. Calcd. C_7H_7NO: C, 69·41; H, 5·82; N, 11·55%); UV max (H_2O) 283 mμ (ε 17,300), 209 mμ (ε 8170); IR (CCl_4) 3095 (w), 3055 (w), 3040 (w), 1650 (m), 1630 (s), 1605 (m), 1537 (m), 1520 (w), 1510 (w), 1465 (vw), 1410 (w), 1365 (w), 1310 (vw), 1230 (m), 1190 (m), 1100 (vw), 1055 (vw), 1040 (vw), 955 (w), 875 (w), 848 (m) and 728 cm^{-1} (m).

N-*Acetyl*-1-*vinylcytosine* (X)

(a) 2,4-Bis(trimethylsilyl)-N^4-acetylcytosine[14] (3g, 0·0106 mole) was refluxed with dry vinyl acetate (17 ml), mercuric acetate (0·2 g), and H_2SO_4 (40 μl) under N_2 for 7 days. At that time TLC indicated no reaction Vinyl acetate (17 ml) was then added and the mixture was placed in a sealed tube under N_2. After heating at 120–140° for 7 days, TLC indicated quantitative conversion to product. The solvent was removed and hot MeOH (20 ml) containing a few drops of NH_4OH was added. After treatment with adsorbing charcoal (Darco G-60) and two recrystallizations from MeOH, N-acetyl-1-vinylcytosine (0·4 g, 21·1%) was obtained as white crystals: m.p. 240–242°. (Found: C, 53·62; H, 5·20; N, 23·29. Calcd. for $C_8H_9N_3O_2$: C, 53·62; H, 5·06; N, 23·45%); UV max (pH7) 312 mμ (ε 9496), 254 mμ (ε 12,848) 220·5 mμ (ε 13,726); IR (nujol 3275 (m), 1710 (m), 1650 (s), 1625 (s), 1560 (s), 1340 (s), 1320 (s), 1275 (w), 1240 (m), 1200 (w), 1190 (m), 1080 (vw), 993 (m), 975 (vw), 960 (vw), 892 (w), 808 (m), 800 (w), and 782 cm^{-1} (m).

(b) 2,4-Bis(trimethylsilyl)cytosine[14] (2·06 g, 0·081 mole) was refluxed with dry vinyl acetate (25 ml), mercuric acetate (0·1 g), and H_2SO_4 (20 μl) under N_2 for 2 days. TLC indicated high conversion to X with smaller amounts of two other products and starting material. The mixture was reduced to dryness, and the remaining residue was recrystallized twice from MeOH yielding white crystals of N-acetyl-1-vinylcytosine (0·2 g, 13·8%): m.p. 240–242. This product was identical with the material prepared in Part A by mixture m.p., TLC and IR spectroscopy.

1-Vinylcytosine (XII)

N-Acetyl-1-vinylcytosine (187 mg, 1·04 m mole) was stirred with 9 ml of methanolic ammonia overnight. TLC indicated quantitative conversion to product. The reaction mixture was reduced to a residue which

was recrystallized from n-propanol yielding white crystals of 1-vinylcytosine (78 mg, 55%): m.p. 217–218°. (Found: C, 52·35; H, 5·53; N, 30·69. Calcd. for $C_6H_7N_3O$; C, 52·54; H, 5·14; N, 30·64%); UV max (pH7) 286 mμ (ε 7019), 240 mμ shoulder, 225 mμ (ε 7101); IR (nujol) 3380 (m), 3150 (m), 1662 (s), 1630 (s), 1520 (m), 1410 (w), 1332 (m), 1285 (m), 1210 (m), 1138 (m), 960 (m), 878 (m), 793 (m), 780 (m), 762 (w) and 715 cm^{-1} (m).

1-*Vinyluracil* (I) *from* 1-*vinylcytosine* (XII)

1-Vinylcytosine (20 mg, 0·146 mmole) in water (1 ml) was stirred for 24 hr with $NaNO_2$ (40 mg) and AcOH (0·2 ml). TLC indicated nearly complete conversion to I. The soln was reduced to dryness and the remaining residue was extracted with boiling toluene (5 ml). White needles of 1-vinyluracil (12 mg, 59·5%) formed on cooling: m.p. 180–182°. This product was identical with authentic I by mixture m.p., IR spectroscopy and TLC.

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