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New Functionalization at the 5-Position of Uracils by Selenenylation

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ABSTRACT

*Electrophilic substitution of phenylselenenyl chloride at the 5-position of uracils in the presence of silver reagents, such as Ag_2O, $AgBF_4$, or CF_3CO_2Ag, afforded the corresponding 5-phenylselenenyluracils in excellent yields. 1,3-Dimethyl-5-phenylselenenyluracil(**2a**), 5-phenylselenenyl-(2',3',5'-tri-O-acetyl)uridine(**2b**), 5-phenylselenoxyl-1,3-dimethyluracil(**3a**) and 5-phenylselenoxyl-(2',3',5'-tri-O-acetyl)uridine(**3b**) were used for various transformations at C-5 or C-6 of pyrimidine bases via nucleophilic substitution, a free radical process, and a Michael-type addition utilizing the unique properties of organo-seleno groups located on C-5 of pyrimidine bases.*

INTRODUCTION

A number of nucleosides incorporating a 5-substituted pyrimidine with a modified sugar attachment are currently undergoing evaluation as antiviral agents [1–3]. In view of the pronounced biological activity, the 5-halogenated pyrimidines were exclusively used as intermediates for a variety of synthetic transformations of related compounds of biological interest, presumably because of the ease of substitution at this position [4]. The most common methods employed for modifying the functional group at the 5-position of a pyrimidine ring have been a photolytic reaction [5] and the palladium-mediated exchange between 5-halogenated pyrimidine derivatives and an organometallic reagent [6] or the use of 5-triflated pyrimidines as the coupling partners for organostannanes [7]. Although the utilization of the lithiation methodology was recently developed for the introduction of a carbon functionality at the C-5 or C-6 position of uridine derivatives [8,9], the ratio (C-5/C-6) of substitution is governed by the substituents on the pyrimidine base and the protecting groups on the sugar.

RESULTS AND DISCUSSION

In new attempts for the functionalization of pyrimidine bases and because of the biological interest of the related compounds, we recently communicated that addition of phenylselenenyl chloride (an electrophilic reagent) to uracils (**1**) in the presence of a silver reagent, such as silver tetrafluoroborate ($AgBF_4$) or silver trifluoroacetate ($AgOCOCF_3$), afforded regioselectively the corresponding 5-phenylselenenylated uracils (**2**) in nearly quantitative yields under mild conditions [10].

The selenenylation can be carried out readily by the reaction of the uracil or the uridine with a silver reagent and phenylselenenyl chloride at ca. 20°C in acetonitrile under mild conditions. The precipitate of AgCl can be removed readily by filtration. The direct phenylselenenylation occurs regioselectively at the C-5 position of uracils or uridines. No 6-substituted products could be obtained: the starting substrate was quantitatively recovered together with diphenyl diselenide after the usual workup. The results obtained are summarized in Table 1. An essential feature of all these procedures is the use of non-nucleophilic and weakly basic counter ions [11], such as BF_4^- and $CF_3CO_2^-$.

Dedicated to Prof. Antonino Fava on the occasion of his seventieth birthday.

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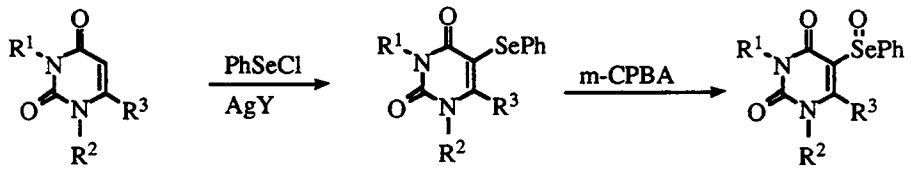
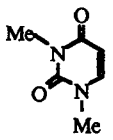
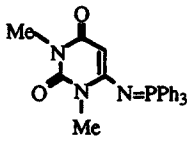
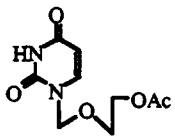
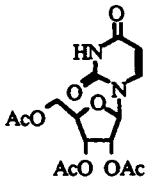
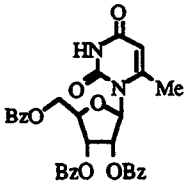


1a : $R^1 = R^2 = Me$, $R^3 = H$
1b : $R^1 = H$, $R^3 = H$
R^2 = (2',3',5',-tri-O-acetyl) β–D-ribofuranosyl

2a : $R^1 = R^2 = Me$, $R^3 = H$
2b : $R^1 = H$, $R^3 = H$
R^2 = (2', 3', 5'-triacetyl) β-D-ribofuranosyl

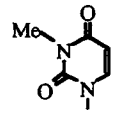
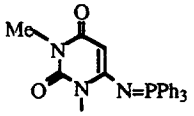
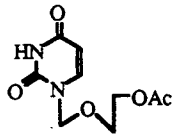
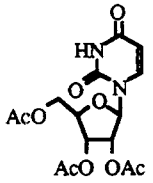
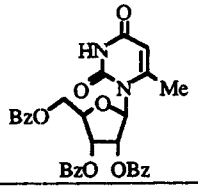
3a : $R^1 = R^2 = Me$, $R^3 = H$
3b : $R^1 = H$, $R^3 = H$
R^2 = (2', 3', 5'-triacetyl) β-D-ribofuranosyl

TABLE 1 Phenylselenenylation at the C-5 Position of Uracils

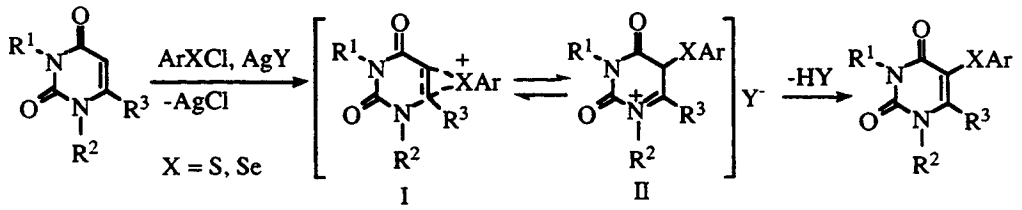
Run	*Uracil*	*AgY*[a]	*Time (h)*	*Temp (°C)*	*Yield*[b] *(%) (2)*
1		Ag_2O	0.5	0	73
2		$AgBF_4$	1	15–20	97
3		$AgBF_4$	1.5	15–20	89
4		$AgOCOCF_3$	2	15–20	99
5		$AgOCOCF_3$	0.25	15–20	95
6		$AgBF_4$	2	15–20	88
7		$AgOCOCF_3$	0.25	15–20	98
8		$AgBF_4$	2	15–20	91
9		$AgOCOCF_3$	0.25	15–20	99

[a]Molar ratio; uracil:PhSeCl:AgY = 1:1.5:1.5.
[b]Isolated yields after chromatographic purification.

TABLE 2 Phenylsulfenylation at C-5 Position of Uracils

Run	Uracil	AgY^a	Time (h)	Temp (°C)	$Yield^b$ (%) (2)
1		$AgBF_4$	0.5	0	89
2		$AgOCOCF_3$	0.5	0	96
3		$AgBF_4$	2	0	47
4		$AgBF_4$	3	0	47
5		$AgBF_4$	2	0	82

[a]Molar ratio; uraci:PhSCl:AgY = 1:1.5:1.5.
[b]Isolated yields after chromatographic purification.



These electrophilic substitution reactions showed a moderate sensitivity to the presence of an electron-releasing group, such as the iminotriphenylphosphorane or the methyl group at the 5-position, resulting in an acceleration of the reaction [11,13], particularly in the phenylsulfenylation one (Table 2, runs 2 and 5). The direct phenylselenenylation reactions are also unusual because common olefins containing the phenylselenenyl group have been obtained by the addition of phenylselenenyl halide to the double bond, followed by hydrogen halide elimination on treatment with a base [12]. The reaction appears to be initiated by an electrophilic addition of a cationoid phenylselenium reagent of the type $PhSe^+Y^-$ which proceeds via the relatively unstable selenium cation intermediate (I) and/or the iminium-ion intermediate (II).

In the phenylselenenylation of compound **4**, the ultimate elimination of HY affords the C-5 substituted uridine derivative (**5**) as the major product. It is reasonable to expect that attack of the electrophilic reagent at C-5 would take place more readily than at C-6 to give the C-5 substituted product exclusively. The relatively unstable cationic intermediate [15] of type (I) would allow nucleophilic attack of the proximate 5′-hydroxyl group to result in the cyclonucleoside (**6**) although it is a minor product.

Organic selenium and sulfur compounds have been utilized for various transformations due to their respective specific properties. Although the

structures of organic selenium compounds are closely related to those of the analogous sulfur compounds, their properties often present marked differences. In the case of cleavage, oxidation, reduction or a free radical process at the carbon-heteroatom bond (C–X, X=S, Se), the use of selenium intermediates is frequently favored by the simpler, milder conditions required [13,17]. Thus, 5-phenylselenenyl-1,3-dimethyluracil (**2a**) and (2′,3′,5′-tri-O-acetyl)uridine (**2b**) as model compounds were used for modification of the pyrimidine base through various transformations, such as nucleophilic substitution, a free radical process, or a Michael-type reaction made possible by some specific properties of the organo-seleno group.

The results obtained are summarized in Table 4. When 5-phenylselenenyl-1,3-dimethyluracil (**2a**) was treated with 2 equivalents of triphenyltin hydride in the presence of azobisisobutyronitrile (AIBN) in refluxing benzene solution, 5-triphenylstannyl-1,3-dimethyluracil was obtained in 92% yield (Table 4, run 1). 1,3-Dimethyluracil, obtained by reduction with triphenyltin hydride, was found only in a trace amount. A similar result was also obtained in the case of **2b** (Table 4, run 2). This intriguing type of organotin-mediated direct deselenative substitution with an organic stannyl radical is unusual and rarely reported [18]. Selenoxides have been widely used as important organoselenium intermediates in which the β-carbon bears a hydrogen atom and which can be decomposed into olefins due to their instability [13,17]. In order to elucidate the utility of a 5-phenylselenoxyluracil, 5-phenylselenenyl-2′,3′-O-isopropylideneuridine as a model compound was treated with m-CPBA and then with triethylamine to afford a cyclonucleoside [14] in 90% overall yield.

The reaction mechanism may be explained as follows: the seleno group is oxidized to selenoxide by m-CPBA and then the 5′-hydroxyl group attacks the activated C-6 position of the pyrimidine base. Then removal of the hydrogen on C-6 by the selenoxyl group, with subsequent elimination of phenylselenenic acid, affords the cyclonucleoside. In a similar manner, the reaction of the selenoxide with amines gave the 6-substituted derivatives through

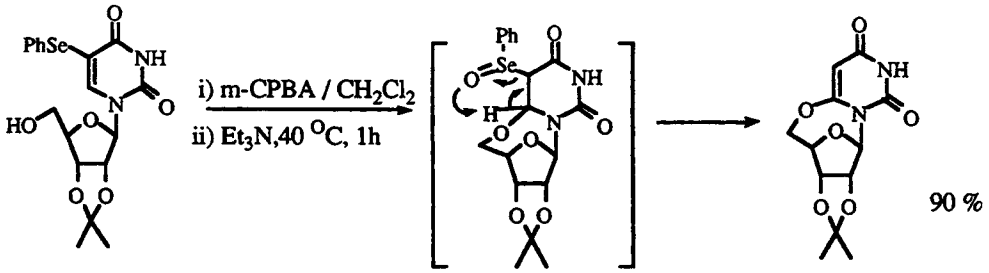
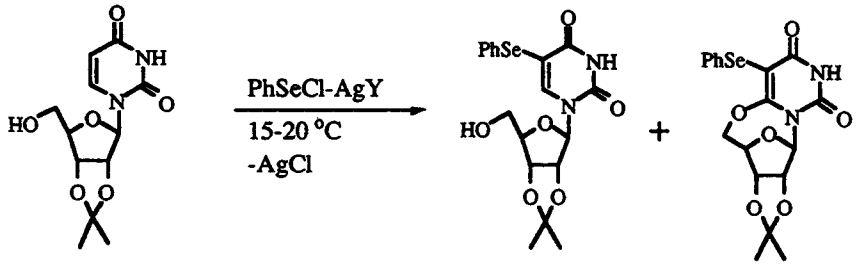


TABLE 3 Reaction of 2′,3′-O-Isopropylideneuridine and PhSeCl

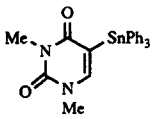
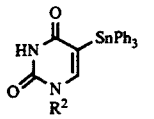
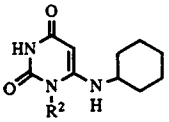
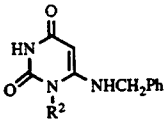
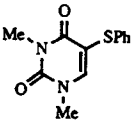
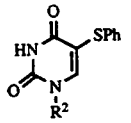
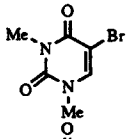
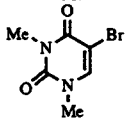
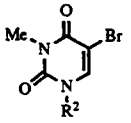


4 5 6

Run	*Solvent*	*AgY*[a]	*Time (h)*	*Yield*[b] *(%) (5/6)*
1	CH_2Cl_2	$AgBF_4$	1	20 (20/trace)
2	MeCN	none	2	trace
3	MeCN	Ag_2O	0.5	85 (85/3)
4	MeCN	$AgBF_4$	0.5	85 (85/2)
5	MeCN	$AgOCOCF_3$	0.25	98 (98/trace)

[a]Molar ratio; *4*:PhSeCl:AgY = 1:2:2.
[b]Isolated yields after chromatographic purification.

TABLE 4 Functionalization at 5- or 6-position of Uracils

Run	Uracil	Reagents	Solvent	Temp (°C)	Time (h)	Products[a]	Yield[b] (%)
1	***2a***	Ph_3SnH-AIBN	Benzene	80	2		92 + ***1a*** (trace)
2	***2b***	Ph_3SnH-AIBN	Benzene	80	2		85 + ***1b*** (9)
3	***3b***	Cyclohexylamine DABCO	THF	15–20	15		76
4	***3b***	Benzylamine DABCO	THF	15–20	10		76
5	***3a***	PhSH-Et_3N	THF	15–20	0.25		96
6	***3b***	PhSH-Et_3N	THF	15–20	0.5		95
7	***3b***	PhSeNa	THF	15–20	0.5	***2b***	70
8	***3a***	HBr	MeCN	15–20	0.1		52 + ***2a*** (36)
9	***3a***	HBr	MeCN	15–20	1		90
10	***3b***	HBr	MeCN	15–20	4		93

[a] R^2 = (2′,3′,5′-tri-O-acetyl)-β-D-ribofuranosyl.
[b] Isolated yield purified by chromatography.

a Michael-type addition-elimination reaction (Table 4, runs 3 and 4). On the other hand, when thiophenol or phenylselenol was used as the nucleophile, the 5-substituted product was obtained in good yield (Table 4, runs 5, 6, and 7). The apparent migration of the thio- or seleno-group from C-6 to C-5 can be understood by the occurrence of successive Michael addition-elimination mechanisms through the 5,6-disubstituted-5,6-dihydrouracil intermediates [16]. It is reasonable to expect that the proton at C-5 would be more acidic than that at C-6 in the intermediates so that the elimination of PhXH (X=S, Se) occurs to give the C-5 substituted products exclusively. Selenenyl substituents are good leaving groups [19] and are readily displaced by a halide ion [20] in good yields (Table 4, runs 8–10). In summary, selenenyl substituents at the C-5 position of uracils may be widely applicable

for modifications of pyrimidines and pyrimidine nucleosides.

EXPERIMENTAL

^{1}H NMR spectra were obtained on a Bruker AM-300 and a Bruker AC-200 spectrometer in $CDCl_3$ solution using tetramethylsilane as an internal standard. IR spectra were taken on a Perkin-Elmer Model 238B and a Bomem MB-100 FT-IR spectrometer. Mass spectra were obtained on a Hewlett Packard GC/MS 5985B instrument. GLC analyses were performed on a Varian 3700 gas chromatograph using a FID detector. All the reactions were monitored by TLC (Merck Kieselgel 60-GF_{254}). Preparative TLC analysis was carried out with Merck silica gel 60-GF_{254}, coated (1.0 mm thickness) on a 20 × 20 cm glass plate. Silica gel used for column chromatography was Merck silica gel (70–230 mesh). All reagents were obtained from Aldrich Chemical Co, Wako Pure Chemical Industries Ltd., or Tokyo Kasei Co. The reagents used and solvents were further purified by general methods.

General Procedure for the Arylselenenylation at the 5-Position of Uracils

To a stirred solution of (2',3',5'-tri-O-acetyl)uridine (185 mg, 0.5 mmol) and silver trifluoroacetate ($AgOCOCF_3$, 144 mg, 0.75 mmol) was added PhSeCl (108 mg, 0.75 mmol) in MeCN (2 mL) at ca. 15–20°C. After stirring for 15 minutes, the resulting silver chloride (AgCl) was filtered off and the filtrate was concentrated and then chromatographed on a short column of silica gel (Merck, column; 2.5 × 5 cm, eluent; CH_2Cl_2:acetone (v/v) = 10:1) to afford the product 5-phenylselenenyl-(2',3',5'-tri-O-acetyl)uridine (258 mg, 98%). ^{1}H NMR ($CDCl_3$, 80 MHz): δ 2.20 (t, 9H, 3 AcH's) 4.35 (br, 3H, H4',5'), 5.35 (m, 2H, H2',3'), 6.10 (d, 1H, H1'), 7.20–7.60 (m, 5H, PhH's), 7.80 (s, 1H, H6); MS (*m/z*) 526 (M^+).

1,3-Dimethyl-5-phenylselenenyluracil

^{1}H NMR ($CDCl_3$): δ 3.60 (s, 3H, NCH_3), 3.65 (s, 3H, NCH_3), 7.35 (s, 5H, PhH's), 7.70 (s, 1H, H6); Ms (*m/z*) 248 (M^+).

5-Phenylseleno-6-[(triphenylphosphoranylidene)amino]-1,3-dimethyluracil

^{1}H NMR ($CDCl_3$): δ 3.50 (s, 3H, NCH_3), 3.77 (s, 3H, NCH_3), 6.70–7.80 (m, 20H, PhH's); MS (*m/z*) 571 (M^+).

1-(2-Acetoxyethoxymethyl)-5-phenylselenenyluracil

^{1}H NMR ($CDCl_3$): δ 2.10 (s, 3H, OAc's), 3.67–4.30 (m, 4H, OCH_2CH_2O), 5.10 (s, 2H, NCH_2), 7.20–7.60 (m, 6H, PhH's); MS (*m/z*) 384 (M^+).

5-Phenylseleno-1-(2',3',5'-tri-O-benzoyl)-6-methyluridine

^{1}H NMR ($CDCl_3$): δ 2.90 (s, 3H, 6-CH_3), 4.85 (br s, 3H, H4',5'), 5.95 (t, 1H, H2'), 6.25 (m, 2H, H1',2'), 7.2–8.2 (m, 20H, PhH's), 9.30 (br s, 1H, NH).

General Procedure for the Phenylsulfenylation at 5-Position of Uracils

To a stirred solution of 1,3-dimethyluracil (70 mg, 0.5 mmol) and $AgBF_4$ (146 mg, 0.75 mmol) in dry MeCN (2 mL) was added PhSCl (108 mg, 0.75 mmol) in MeCN (2 mL) at 0°C. After stirring for 30 minutes, the reaction mixture was filtered. The filtrate was concentrated and purified by short column chromatography on silica gel (column: 2.5 × 5 cm, eluent; CH_2Cl_2:acetone = 20:1) to give the product (110 mg, 89% yield). ^{1}H NMR ($CDCl_3$): δ 3.60 (s, 3H, NCH_3), 3.65 (s, 3H, NCH_3), 7.35 (s, 5H, PhH's), 7.70 (s, 1H, H6); MS (*m/z*) 248 (M^+).

5-Phenylsulfydryl-6-[9-triphenylphosphoranylidene)amino]-1,3-dimethyluracil

^{1}H NMR ($CDCl_3$): δ 3.43 (s, 3H, NCH_3), 3.77 (s, 3H, NCH_3), 6.50–7.80 (m, 20H, PhH's); MS (*m/z*) 523 (M^+).

1-(2-Acetoxyethoxymethyl)-5-phenylselenenyluracil

^{1}H NMR ($CDCl_3$): δ 2.18 (s, 3H, OAc's), 3.80–5.50 (m, 4H, OCH_2CH_2O), 5.33 (s, 2H, NCH_2), 7.40 (br s, 6H, PhH's), 7.80 (s, 1H, H6).

5-Phenylsulfydryl-1-(2',3',5'-tri-O-acetyl)uridine

^{1}H NMR ($CDCl_3$): δ 2.30 (t, 9H, 3 AcH's), 4.48 (br s, 3H, H4',5'), 5.50 (m, 2H, H2',3'), 6.20 (d, 1H, H1'), 7.38 (m, 5H, PhH's), 7.98 (s, 1H, H6), 9.40 (br s, 1H, NH).

5-Phenylsulfydryl-1-(2',3',5'-tri-O-benzoyl)-6-methyluridine

^{1}H NMR ($CDCl_3$): δ 2.78 (s, 3H, 6-CH_3), 4.80 (br s, 3H, H4',5'), 5.90–6.20 (m, 3H, H1',2',3'), 7.10–8.20 (m, 20H, PhH's).

Reaction of 2',3'-O-isopropylideneuridine with Phenylselenenyl Chloride

A mixture of 2',3'-O-isopropyledeneuridine (142 mg, 0.5 mmol), PhSeCl (144 mg, 0.75 mmol), and $AgBF_4$

(146 mg, 0.75 mmol) was stirred for 1 hour at 15–20°C in dry MeCN (4 mL). The reaction mixture was filtered and the filtrate was concentrated. The residue was purified by the preparative TLC on silica gel (eluent; CH_2Cl_2:MeOH = 10:1) to give 5-phenylseleno-2',3'-O-isopropylidene uridine (**4**, 83% yield) and 5-phenylseleno-5,6-anhydro-2',3'-O-isopropyledene-6-hydroxyuridine (**5**, 2% yield).

4: IR (KBr) 3475, 3200, 1694, 1442, 1271, 1087 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.48, 1.70 (d, 6H, two CH_3), 3.80 (m, 3H, H4', H5'), 3.80 (br s, 1H, 5'-OH), 5.00 (m, 2h, H2', H3'), 5.76 (d, 1H, H6), 6.58 (s, H, H1'); MS (*m/z*) 440 (M^-).

5: ^1H NMR ($CDCl_3$): δ 1.34, 1.52 (d, 6H, two CH_3), 3.65, 4.35 (dd, $J_{4',5'}$ = 12 Hz, 2H, H5'), 4.52 (s, 1H, H4'), 4.85 (m, 2H, H2',3'), 6.57 (s, 1H, H1'), 7.10–7.50 (m, 5H, PhH's), 9.05 (br, 1H, NH); MS (*m/z*) 438 (M^+).

Reaction of 5-Phenylseleno-1,3-dimethyluracil with Triphenyltin Hydride

To a stirred solution of 5-phenylseleno-1,3-dimethyluracil (89 mg, 0.3 mmol) and AIBN (5 mg, 0.03 mmol) in degassed dry benzene (4 mL) was added Ph_3SnH (210.6 mg, 0.6 mmol), and then the solution was heated at 80°C for 2 hours under argon. The resulting reaction mixture was filtered and the filtrate washed with CH_2Cl_2 (10 mL), concentrated in vacuo, and then chromatographed on a column of silica gel (eluent; CH_2Cl_2:acetone = 30:1) to afford 5-triphenylstannyl-1,3-dimethyluracil (135 mg, 92% yield) and a trace amount of 1,3-dimethyluracil. ^1H NMR ($CDCl_3$): δ 3.38, 4.50 (d, 9H, NCH_3), 7.50 (s, 1H, H6), 7.30–7.90 (m, 15H, PhH's).

Reaction of 5-Phenylseleno-1-(2',3',5'-tri-O-acetyl)uridine with Triphenyltin Hydride

The reaction was performed as in the previously described experiment. The reaction mixture was purified by preparative TLC on silica gel (eluent; CH_2Cl_2:MeOH = 25:1) to give the product of 5-triphenylstannyl-1-(2',3',5'-tri-O-acetyl)uridine (85% yield) as a foam and (2',3',5'-tri-O-acetyl)uridine (93% yield). ^1H NMR ($CDCl_3$): δ 2.20 (t, 9H, OAc's), 4.10–4.30 (m, 3H, H4',5'), 5.20–5.35 (m, 2H, h2',3'), 6.10 (d, 1H, H1'), 7.30–7.80 (m, 16H, H6, PhH's), 9.50 (br s, 1H, NH).

Synthesis of 5-Phenylselenoxyl-1,3-dimethyluracil

To a solution of 5-phenylseleno-1,3-dimethyluracil (296 mg, 1 mmol) in CH_2Cl_2 (5 mL) was added m-CPBA (287 mg, 60%) at 0°C with stirring. After 30 minutes, the reaction mixture was adjusted to pH 8 with dilute $NaHCO_3$ solution and extracted with CH_2Cl_2 (30 mL × 3). The organic layer was evaporated to dryness to afford the product as a white solid (308 mg, 98% yield). ^1H NMR ($CDCl_3$): δ 3.45, 3.65 (d, 6H, NCH_3), 7.50–8.10 (m, 5H, PhH's), 7.90 (s, 1H, H6).

Synthesis of 5-Phenylselenoxyl-1-(2',3',5'-tri-O-acetyl)uridine

The reaction was performed as in the previously described experiment. The product was obtained by the chromatography on a short column of silica gel (eluent; CH_2Cl_2:MeOH = 25:1 96% yield). ^1H NMR ($CDCl_3$): δ 2.20 (t, 9H, OAc's), 4.20 (br s, 3H, H4',5'), 5.30–5.62 (m, 2H, H2',3'), 6.10 (s, 1H, H1'), 7.40–8.00 (m, 5H, PhH's), 8.18 (s, 1H, H6).

Synthesis of 5',6-Anhydro-2',3'-O-isopropylidene-6-hydrouridine

To a solution of 5-phenylselenenyl-2',3'-O-isopropylideneuridine (88 mg, 0.2 mmol) in CH_2Cl_2 (4 mL) was added m-CPBA (50 mg, 60%) at 0°C with stirring. After stirring for 15 minutes, the reaction mixture was treated with Et_3N (0.5 mL) and then heated at 40°C for 1 hour. The mixture was chromatographed on a silica gel (eluent; CH_2Cl_2:acetone = 3:1) to afford the product (48 mg, 90% yield). ^1H NMR ($CDCl_3$): δ 1.35, 1.55 (d, 6H, CH_3), 4.01, 4.62 (dd, 2H, H5'), 4.90 (d, 1H, H3'), 4.98 (d, 1H, H2'), 5.30 (s, 1H, H5), 6.27 (s, 1H, H1'), 11.40 (br s, 1H, NH).

Synthesis of 6-Benzylamino-1-(2',3',5'-tri-O-acetyl)uridine

A mixture of 5-phenylselenoxy-1-(2',3',5'-tri-O-acetyl)uridine (53 mg, 0.1 mmol), DABCO (22.4 mg, 0.2 mmol), and benzylamine (32 mg, 0.3 mmol) was stirred in dry THF (2 mL) for 10 hours at room temperature. The reaction mixture was concentrated in vacuo and then purified by the preparative TLC on silica gel (eluent; CH_2Cl_2) to give the product (37 mg, 78% yield). ^1H NMR ($CDCl_3$): δ 2.00 (t, 9H, OAc's), 4.0–4.50 (m, 5H, H4',5', CH_2), 5.30–6.00 (m, 4H, H2',3', H5), 7.00–7.40 (m, 5H, PhH's).

Synthesis of (2',3',5-Tri-O-acetyl)-5-bromouridine

To a solution of 5-phenylselenoxyl-1-(2',3',5'-tri-O-acetyl)uridine (54 mg, 0.1 mmol) in MeCN (2 mL) was slowly added HBr (50 mg, 0.3 mmol, 48%) in MeCN (1 mL) at room temperature. After stirring for 4 hours, the solution was neutralized with dilute $NaHCO_3$ solution and then extracted with CH_2Cl_2 (20 mL × 3), dried over $MgSO_4$, and concentrated in vacuo. The residue was chromatographed on a column of silica gel (eluent; CH_2Cl_2:MeOH = 20:1) to afford the product (42 mg) in 93% yield. ^1H NMR ($CDCl_3$): δ 2.20 (t, 9H, OAc's),

4.45 (br s, 3H, H4',5'), 5.40 (m, 2H, h2',3'), 6.20 (d, 1H, H1'), 7.90 (s, 1H, H6).

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