Pergamon

Tetrahedron, Vol. 52, No. 8, pp. 2827-2838, 1996

0040-4020/96 $15.00 + 0.00

S0040-4020(96)00004-X

A FACILE AND REGIO- AND STEREO-SELECTIVE PREPARATION OF BICYCLIC GUANIDINES BY IODOCYCLIZATION OF 3-(ALK-2-ENYL)-2-(SUBSTITUTED AMINO)-1-IMIDAZOLIN-4-ONES[1]

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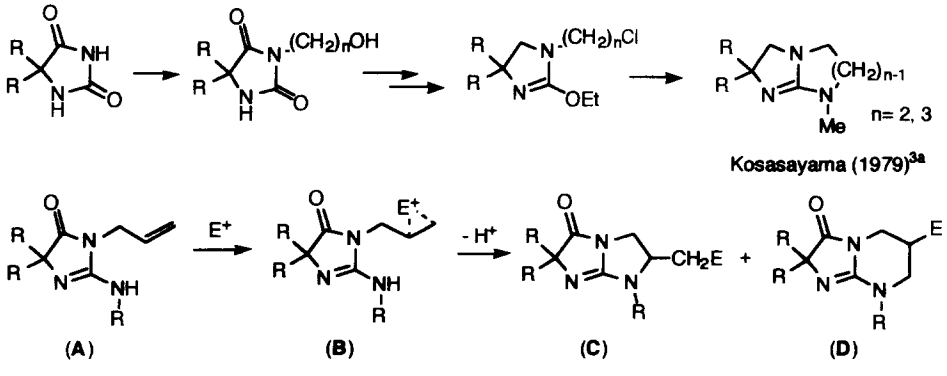
Abstract: The iodocyclization of 3-(alk-2-enyl)-2-(substituted amino)-1-imidazolin-4-ones proceeded in regio- and stereo-selective manners to give bicyclic guanidines, imidazo[1,2-*a*]-imidazole and/or imidazo[1,2-*a*]pyrimidine, in good yields. The regiochemistry of the cyclization depended mainly on the kind of substituents of the alkenyl moieties and was interpretable by the PM3 MO calculations of the iodonium ion intermediates.

Although some bicyclic guanidine derivatives, imidazo[1,2-*a*]imidazole and imidazo[1,2-*a*]pyrimidine, showed a potent hypoglycemic activity,[2] the synthetic routes have been considerably limited (Scheme 1).[3] In order to elucidate the synthetic utilities of functionalized carbodiimides, we examined to prepare 3-alkenyl-2-(substituted amino)-1-imidazolin-4-ones (**A**) by the reaction of ethyl 2-methyl-2-(*N'*-substituted)carbodiimido-propionate with alkenylamines.[4] Intramolecular nucleophilic attack to the activated alkene moiety of the imidazolinones was expected to provide a new route to imidazo[1,2-*a*]imidazole (**C**) and imidazo[1,2-*a*]-pyrimidine derivatives (**D**) (Scheme 1). Much attention has been concentrated on the cyclizations utilizing iodine

Scheme 1.



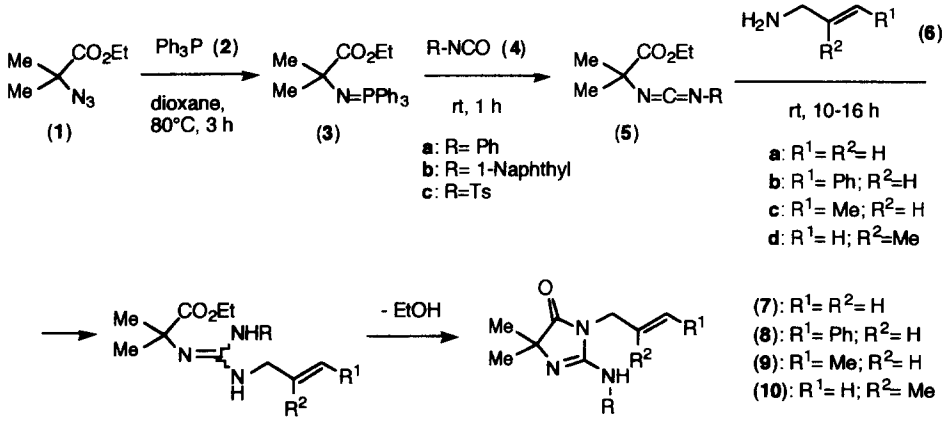
as the activating trigger (iodocyclizations) and their application to the regio- and stereo-selective synthesis of nitrogen containing heterocycles was found in the literatures.[5] It has been described that the regio- and stereo-selectivity on the cyclizations was attributed to the formation of the iodonium ion intermediates and to their opening with nucleophiles. The regioselectivity of the iodocyclization has been interpreted by Baldwin rule[6] and, however, discussions on the regioselectivity using molecular orbital (MO) calculations of the iodonium ions have not been made enough. In the present paper, we describe the facile preparation of the bicyclic guanidines by the iodocyclization of 3-(alk-2-enyl)-2-(substituted amino)-1-imidazolin-4-ones. The iodocyclization

proceeds in a highly stereoselective manner and its regioselectivity will be discussed by the PM3 MO calculations of the iodonium ions.

Iodocyclization of 3-(Alk-2-enyl)-2-(substituted amino)-1-imidazolin-4-ones

The Staudinger reaction of ethyl 2-azido-2-methylpropionate (**1**) with triphenylphosphine (**2**) in dioxane at 80 °C for 1 h gave an iminophosphorane **3**, which was allowed to react with phenyl isocyanate (**4a**) at room temperature for 1 h to give carbodiimide **5a**. To the reaction mixture allylamine (**6a**) was added and the resulting mixture was stirred at room temperature for 10 h. These one-pot procedures and column separation on silica gel afforded 3-allyl-2-anilino-5,5-dimethyl-1-imidazolin-4-one (**7a**) in 66% yield. Similarly, 3-allyl-2-(1-naphthylamino)- (**7b**) and 3-allyl-2-tosylamido-5,5-dimethyl-1-imidazolin-4-one (**7c**) were prepared in 60 and 88% yields, respectively. Other 3-(*trans*-cinnamyl)- **8**, 3-(*trans*-but-2-enyl)- **9**, and 3-methallyl-2-(substituted amino)-1-imidazolin-4-ones **10** were also obtained in moderate to good yields (Scheme 2 and see the Experimental section).

Scheme 2. One-pot Procedures for the Preparation of 3-(Alk-2-enyl)-5,5-dimethyl-2-(substituted amino)-1-imidazolin-4-ones **7-10**



Scheme 3.

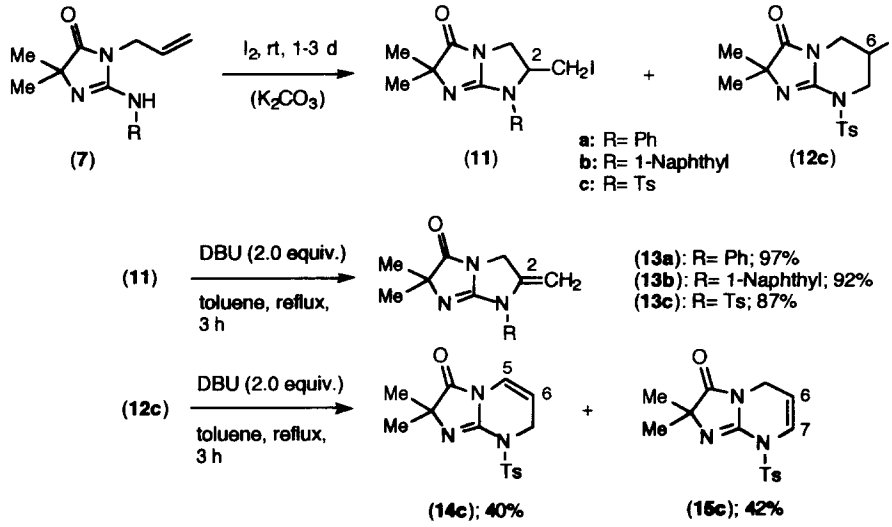


Table 1. Reaction of 3-Allyl-5,5-dimethyl-2-(substituted amino)-1-imidazolin-4-ones **7** with Iodine.

Entry	Substrate	R	Solvent	K_2CO_3 (equiv.)	Time	Product (Yield; %)[a]
1	**7a**	Ph	DME	none	1 d	**11a** (65)
2	**7a**	Ph	DME	(2.0)	3 h	**11a** (98)
3	**7b**	1-Naphthyl	DME	none	1 d	**11b** (80)
4	**7b**	1-Naphthyl	DME	(2.0)	1 d	**11b** (83)
5	**7c**	Ts	DME	none	3 d	**11c** (79) **12c** (9)
6	**7c**	Ts	DME	(2.0)	3 d	**7c** (70) **11c** (21) **12c** (4)
7	**7c**	Ts	MeCN	none	3 d	**11c** (74) **12c** (8)

[a] Isolated yield.

The reaction of imidazolinone **7a** with iodine (3.0 equiv.) in dimethoxyethane (DME) at room temperature for 1 day gave an imidazo[1,2-*a*]imidazole **11a** in 65% yield. The effect of the solvents utilized was also examined; the similar reaction in THF (62%) and acetonitrile (MeCN; 58%) gave almost same results. However, the addition of potassium carbonate (K_2CO_3, 2.0 euiv.) into the DME solution resulted in a significant improvement of the formation of product **11a** (Table 1, entry 2). The structural assignment of product **11a** was accomplished by its analytical and spectroscopic data; its ^{13}C NMR spectrum showed six sp^3-carbon signals, the signal at the highest field (δ= 7.23) of which was confirmed to be methylene carbon one by DEPT measurements and, therefore, deduced to be iodomethyl carbon signal due to the heavy atom effect of iodine atom.[7] The formation of **11a** is defined as a 5-*exo* cyclization by Baldwin rule.[6] The similar reaction of imidazolinone **7b** in DME with and without K_2CO_3 gave also a 5-*exo* cyclization product **11b** in 83% and 80% yield, respectively. A slightly different results were found in the reaction of imidazolinone **7c** with iodine; 6-*endo* cyclization product **12c**, imidazo[1,2-*a*]pyrimidine, was obtained as a minor together with 5-*exo* one **11c** (Scheme 3). Utilization of K_2CO_3 in the similar reaction of **7c** afforded only negative results. The structure of product **12c** was also deduced by its ^{13}C NMR spectrum; the methine carbon signal at the highest field (δ= 12.10) was assigned to be iodometheylene carbon one at the 6-position. The structures of products **11a-c** and **12c** were confirmed by the treatment with DBU in refluxing toluene; while 5-*exo* products **11** gave *exo*-methylene products **13** with the elimination of hydrogen iodide in excellent yields, 6-*endo* one **12c** gave regioisomeric **14c** and **15c** in good total yields (Scheme 3). Next our concern was focused on the regiochemistry of the iodocyclization and the similar

Scheme 4.

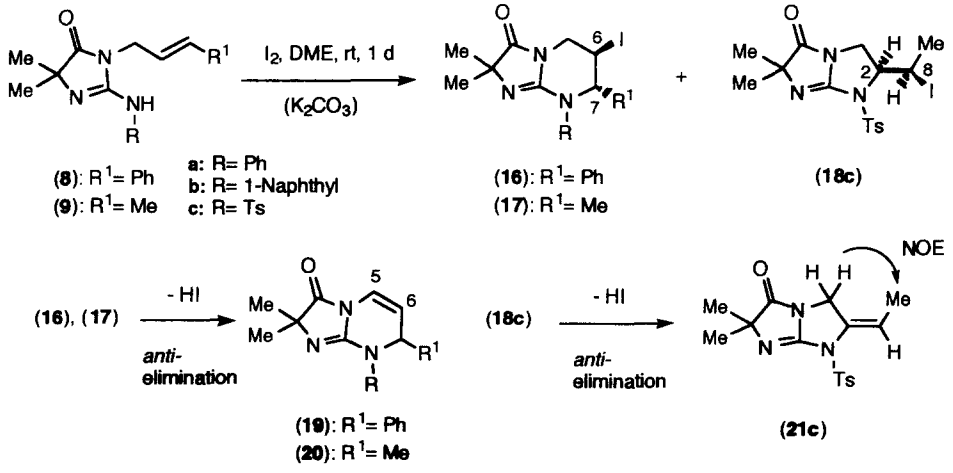


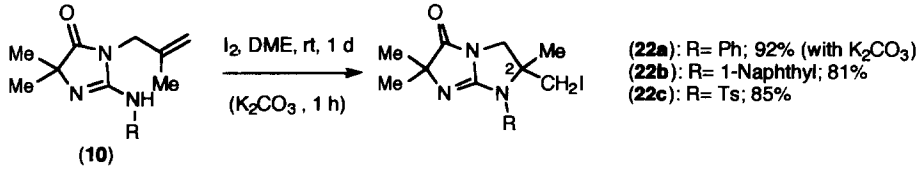
Table 2. Iodocyclization of 3-(*trans*-Cinnamyl)- **8** and 3-(*trans*-But-2-enyl)-5,5-dimethyl-2-(substituted amino)-1-imidazolin-4-ones **9** in DME at Room Temperature.

Entry	Substrate	R	R^1	K_2CO_3 (equiv.)	Time	Product (Yield: %)[a]
1	**8a**	Ph	Ph	none	1 d	**16a** (80)
2	**8a**	Ph	Ph	2.0	3 h	**16a** (94)
3	**8b**	1-Naphthyl	Ph	none	1 d	**16b** (90)
4	**8c**	Ts	Ph	none	1 d	**16c** (77)
5	**9a**	Ph	Me	none	1 d	**17a** (35)[b]
6	**9a**	Ph	Me	2.0	3 h	**17a** (96)
7	**9c**	Ts	Me	none	1 d	**17c** (89) **18c** (3)

[a] Based on isolated products. [b] A mixture of unidentified products was also obtained.

reaction of 3-(*trans*-cinnamyl)- **8** and 3-(*trans*-but-2-enyl) substrates **9** was examined; imidazolinones **8a-c** gave 6-*endo* products **16a-c** as single diastereoisomers in good yields (Scheme 4). The structures of products **16** were assigned on the basis of their ^{13}C and ^1H NMR spectra and the configuration between the 5- and 6-H was confirmed unambiguously to be *trans* by X-ray crystallographic study of **16a**.[8] Imidazolinones **9a,c** in the similar conditions gave 6-*endo* products **17a,c** and 5-*exo* one **18c** as a minor (Scheme 4). The stereochemistry of **17a** was also confirmed by X-ray crystallographic study.[8] These suggest that the formation of iodonium ion proceeds with the retention of the configuration of alkenyl moiety and the successive nucleophilic opening of the ion by the amino nitrogen does in the S_N2 manner with the inversion of configuration at the reaction site. The elimination of hydrogen iodide from the 6-*endo* product **16** and **17** was of much interest; both gave 7,8-dihydroimidazo[1,2-*a*]pyrimidin-3(2*H*)-one derivatives **19** and **20**, respectively, which were formed by the *anti*-elimination of hydrogen iodide. Similar *anti*-elimination of hydrogen iodide from the 5-*exo* product **18c** gave an ethylidene product **21c** with *E*-configuration (Scheme 4). The reaction of 3-methallyl substrates **10a-c** with iodine gave exclusively 5-*exo* cyclization products **22a-c** in good yields (Scheme 5).

Scheme 5.

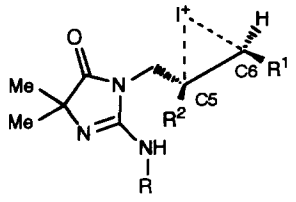


(10)

Regiochemistry of the Iodocyclizations: Discussions Utilizing PM3 MO Calculations of the Iodonium Ion Intermediates

As mentioned above, the reactivity and regiochemistry of these iodocyclizations were interpretable in the terms of the interaction between the LUMO of the iodonium ion and the HOMO of the amino nitrogen. However, MO calculation data of iodonium ions have been rare in the literatures[9] and we attempted to use MO calculation results in order to elucidate qualitatively the regiochemistry. According to the preceding studies on the MO calculations of bromonium ions,[10] no significant differences were found between the PM3 and *ab initio* calculations.[10b] We, therefore, underwent the MO calculations of two types of the iodonium ions by PM3 method[11] in MOPAC program;[12] one of which was 2-anilino (**a**: R= Ph) and the other was 2-tosylamido (**c**: R=Ts) iodonium ions. While the coefficients of HOMO of the anilino-type iodonium ions were located at the anilino nitrogen and the phenyl carbons, those of the tosylamido-type ones at the three nitrogen atoms of imidazolinone and tosylamido moieties. The coefficients of LUMO of both the iodonium ions were located at both the bridgehead carbon atoms and iodine of the ions. The effects of the substituents of the alkenyl moieties

Table 3. Energy Levels of the Frontier Orbitals of the Iodonium Ions **23-26** and Their Frontier Electron Density for Nucleophile fr(N) in the 5-*exo* and 6-*endo* Cyclizations.



(**23**): R^1= R^2= H
(**24**): R^1= Ph; R^2= H
(**25**): R^1= Me; R^2= H
(**26**): R^1= H; R^2= Me

a: R= Ph; **c**: R= Ts

					Energy Level/eV		Frontier Electron Density for Nucleophile fr(N)	
Entry	Iodonium Ion	R	R^1	R^2	HOMO	LUMO	C5-*exo*	C6-*endo*
1	**23a**	Ph	H	H	- 11.772	- 6.542	0.495	0.321
2	**23c**	Ts	H	H	- 12.440	- 6.717	0.387	0.417
3	**24a**	Ph	Ph	H	- 11.638	- 6.131	0.116	0.694
4	**24c**	Ts	Ph	H	- 12.237	- 5.763	0.131	0.683
5	**25a**	Ph	Me	H	- 11.757	- 6.444	0.419	0.425
6	**25c**	Ts	Me	H	- 12.379	- 5.917	0.388	0.459
7	**26a**	Ph	H	Me	- 11.822	- 6.418	0.559	0.288
8	**26c**	Ts	H	Me	- 12.237	- 5.763	0.540	0.310

on the regiochemistry of cyclization were also examined. The frontier electron density for nucleophile fr(N) in the 5-*exo* and 6-*endo* cyclization and the HOMO and LUMO energy levels of the iodonium ions are summarized in Table 3. The iodonium ion **23a** (R= Ph) from imidazolinone **7a** had a larger fr(N) value for 5-*exo* cyclization (0.495) than that for 6-*endo* one (0.321) and, therefore, the preference of the 5-*exo* cyclization in **23a** was understood taking the stereoelectronic effects cited by Baldwin into consideration. On the other hand, the fr(N) values of the iodonium ion **23c** (R= Ts) were C5-*exo* (0.387) and C6-*endo* (0.417), respectively, and the 6-*endo* cyclization took place in competition with the 5-*exo* one. The preferences of the 6-*endo* cyclization for 3-cinnamyl substrates **8** and of 5-*exo* one for 3-methallyl substrates **10** were also understood by the PM3 calculation results of the iodonium ions **24** and **26**. While the fr(N) values of iodonium ion **25c** showed the preference of the 6-*endo* cyclization, those of iodonium ion **25a** were almost equal, C5-*exo* (0.419) and C6-*endo* (0.425), and suggested a little preference of the 5-*exo* one from the Baldwin's rule.[6] However, the 6-*endo* cyclization product **17a** was formed exclusively in the reaction of **9a** with iodine.

Conclusion

The iodocyclization of 3-(alk-2-enyl)-2-(substituted amino)-1-imidazolin-4-ones gave the bicyclic guanidine derivatives in regio- and stereo-selective manners. The regiochemistry of the cyclization was controlled by the kinds of substituents on the both the alkenyl and 2-amino moieties. The PM3 MO calculations of the iodonium ion intermediates were available to interpret the regiochemistry. Further investigations on the reaction path and scope of the iodocyclization are in progress in our laboratory.

Experimental

General. For general details of apparatuses and procedures, see the previous paper.[13] ^{1}H and ^{13}C NMR spectra were measured on JEOL EX-270 spectrometer (at 270 MHz for ^{1}H and 68 MHz for ^{13}C) in deuteriochloroform ($CDCl_3$) solution, unless otherwise stated. Assignment of the NMR spectra of products was accomplished by ^{1}H-^{1}H and ^{1}H-^{13}C COSY spectra. Overlapping splitting patterns in ^{1}H NMR spectra are

indicated as ov. Ethyl 2-azido-2-methylpropionate (**1**) was obtained quantitatively by the reaction of ethyl 2-bromo-2-methylpropionate with sodium azide (2.0 equiv.) in 20%-aqueous methanol at 50 °C for 2 d; colorless oil, IR (neat) 2100 (N_3), 1735 cm^{-1} (CO); ^1H NMR δ= 1.32 (3 H, t, *J*= 7.3 Hz, CH_2CH_3), 1.47 (6 H, s, Me), 4.25 (2 H, q, *J*= 7.3 Hz, CH_2CH_3). Alkenylamine **6b-d** were obtained by the treatment of the corresponding hydrochlorides[14] with an excess of triethylamine *in situ*.

Preparation of 1-Imidazolin-4-ones 7, 8, 9, and 10. General Procedures: To a solution of azide **1** (0.189 g, 1.2 mmol) in dry dioxane (5 ml) heated at 80 °C under argon atmosphere was added triphenylphosphine (**2**; 0.262 g, 1.0 mmol) in dry dioxane (5 ml) and immediately nitrogen was extruded. The reaction mixture was stirred for 3 h at the same temperature and cooled down to room temperature. Phenyl isocyanate (**4a**; 0.109 ml, 1.0 mmol) was added and stirred for 1 h. *trans*-Cinnamylamine hydrochloride (0.255 mg, 1.5 mmol) and triethylamine (0.28 ml, 2.0 mmol) were added to the mixture and stirred at room temperature for 11 h. The solvent was evaporated to dryness, which was extracted with dichloromethane (3 x 15 ml) and the organic layer was washed with water and dried on anhydrous magnesium sulfate. The solvent was evaporated and the residue was subjected to column chromatography on silica gel to give imidazolinone **8a** (0.163 g, 51%) with hexane/ethyl acetate (5/1). Similarly, other 1-imidazolin-4-ones **7**, **8**, **9**, and **10** were prepared and their structures were fully confirmed by the analytical and spectral data, the selective data of which, the yield, mp and ^1H NMR and analytical data, are summarized as follows.

3-Allyl-2-anilino-5,5-dimethyl-1-imidazolin-4-one (**7a**): yield 54%; mp 103-105 °C; ^1H NMR δ= 1.37 (6 H, s, Me), 4.26 (2 H, d, *J*= 5.5 Hz, CH_2), 4.76 (1 H, br s, NH), 5.20 (1 H, dd, *J*= 1.5, 9.9 Hz, =CH*H*), 5.25 (1 H, dd, *J*= 1.5, 17.6 Hz, =C*H*H), 5.94 (1 H, m, -CH=), 6.96, 7.03, 7.31 (total 5 H, Ph). Anal. Found: C, 69.38; H, 7.09; N, 17.49%. Calcd for $C_{14}H_{17}N_3O$: C, 69.11; H, 7.04; N, 17.27%.

3-Allyl-5,5-dimethyl-2-(1-naphthylamino)-1-imidazolin-4-one (**7b**): yield 48%; mp 166-167 °C; ^1H NMR δ= 1.33 (6 H, s, Me), 4.40 (2 H, d, *J*= 5.6 Hz, CH_2), 4.66 (1 H, br s, NH), 5.29 (1 H, dd, *J*= 1.3, 10.2 Hz, =CH*H*), 5.35 (1 H, dd, *J*= 1.3, 15.5 Hz, =C*H*H), 6.05 (1 H, m, -CH=), 7.01, 7.37-7.46, 7.56, 7.83, 8.01 (total 7 H, naphthyl-H). Anal. Found: C, 73.94; H, 6.60; N, 14.31%. Calcd for $C_{18}H_{19}N_3O$: C, 73.69; H, 6.53; N, 14.33%.

3-Allyl-5,5-dimethyl-2-tosylamido-1-imidazolin-4-one (**7c**): yield 88%; mp 133-134 °C; ^1H NMR δ= 1.44 (6 H, s, Me), 2.42 (3 H, s, Me), 4.11 (2 H, d, *J*= 6.6 Hz, CH_2), 5.10 (1 H, dd, *J*= 1.1, 16.1 Hz, =CH*H*), 5.11 (1H, dd, *J*= 1.1, 9.9 Hz, =C*H*H), 5.73 (1 H, m, =CH-), 7.29, 7.82 (total 4 H, aromatic-H), 8.02 (1 H, br, NH). Anal. Found: C, 56.00; H, 5.96; N, 13.07%. Calcd for $C_{20}H_{21}N_3O$: C, 56.05; H, 5.96; N, 13.08%.

2-Anilino-3-(*trans*-cinnamyl)-5,5-dimethyl-1-imidazolin-4-one (**8a**): yield 51%; mp 112-113 °C; ^1H NMR δ= 1.37 (6 H, s, Me), 4.41 (2 H, d, *J*= 6.6 Hz, CH_2), 4.75 (1 H, br s, NH), 6.34 (1 H, td, *J*= 6.6, 16.1 Hz, CH_2-C*H*=), 6.67 (1 H, d, *J*= 16.1 Hz, =C*H*-Ph), 6.97-7.08, 7.22-7.41 (total 10 H, Ph). Anal. Found: C, 75.13; H, 6.67; N, 12.99%. Calcd for $C_{20}H_{21}N_3O$: C, 75.21; H, 6.63; N, 13.16%.

3-(*trans*-Cinnamyl)-5,5-dimethyl-2-(1-naphthylamino)-1-imidazolin-4-one (**8b**): yield 46%; mp 123-124 °C; ^1H NMR δ= 1.36 (6 H, s, Me), 4.56 (2 H, d, *J*= 6.2 Hz, CH_2), 4.66 (1 H, br s, NH), 6.44 (1 H, td, *J*= 6.2, 16.1 Hz, CH_2-C*H*=), 6.78 (1 H, d, *J*= 16.1 Hz, =C*H*-Ph), 7.04, 7.23-7.49, 7.57, 7.82, 8.03 (total 12 H, aromatic-H). Anal. Found: C, 78.20; H, 6.37; N, 11.45%. Calcd for $C_{24}H_{23}N_3O$: C, 78.02; H, 6.28; N, 11.37%.

3-(*trans*-Cinnamyl)-5,5-dimethyl-2-tosylamido-1-imidazolin-4-one (**8c**): yield 84%; mp 157-158 °C; ^1H NMR δ= 1.44 (6 H, s, Me), 2.37 (3 H, s, Me), 4.26 (2 H, d, *J*= 6.6 Hz, CH_2), 6.06 (1 H, td, *J*= 6.6, 16.1 Hz, CH_2-C*H*=), 6.48 (1 H, d, *J*= 16.1 Hz, =C*H*-Ph), 7.17-7.28, 7.81 (total 9 H, aromatic-H), 8.05 (1 H, br s, NH). Anal. Found: C, 63.65; H, 5.82; N, 10.56%. Calcd for $C_{21}H_{23}N_3O_3S$: C, 63.45; H, 5.83; N, 10.57%.

2-Anilino-3-(*trans*-but-2-enyl)-5,5-dimethyl-1-imidazolin-4-one (**9a**): yield 44%; mp 86-88 °C; ^1H NMR δ= 1.36 (6 H, s, Me), 1.70 (3 H, d, *J*= 6.3 Hz, =CH-*Me*), 4.19 (2 H, d, *J*= 5.6 Hz, CH_2), 4.68 (1 H, br s,

NH), 5.60 (1 H, td, *J*= 5.6, 16.8 Hz, CH_2-C*H*=), 5.75 (1 H, qd, *J*= 6.3, 16.8 Hz, =C*H*-Me), 6.98, 7.03, 7.31 (total 5 H, Ph). Anal. Found: C, 70.10; H, 7.55; N, 16.28%. Calcd for $C_{15}H_{19}N_3O$: C, 70.01; H, 7.44; N, 16.33%.

3-(*trans*-But-2-enyl)-5,5-dimethyl-2-tosylamido-1-imidazolin-4-one (**9c**): yield 82%; mp 157-158 °C; ^{1}H NMR δ= 1.42 (6 H, s, 5-Me), 1.59 (3 H, d, *J*= 6.3 Hz, =CH-*Me*), 2.42 (3 H, s, Me), 4.03 (2 H, d, *J*= 6.3 Hz, CH_2), 5.37 (1 H, td, *J*= 6.3, 16.8 Hz, CH_2-C*H*=), 5.61 (1 H, qd, *J*= 6.3, 16.8 Hz, =C*H*-Me), 7.30, 7.83 (total 4 H, aromatic-H), 8.02 (1 H, br s, NH). Anal. Found: C, 57.23; H, 6.37; N, 12.53%. Calcd for $C_{16}H_{21}N_3O_3S$: C, 57.30; H, 6.31; N, 12.53%.

2-Anilino-3-methallyl-5,5-dimethyl-1-imidazolin-4-one (**10a**): yield 48%; mp 96-97 °C; ^{1}H NMR δ= 1.38 (6 H, s, 5-Me), 1.80 (3 H, s, Me), 4.19 (2 H, s, CH_2), 4.74 (1 H, br s, NH), 4.80, 4.90 (each 1 H, each s, =CH_2), 6.94, 7.04, 7.29 (total 5 H, Ph). Anal. Found: C, 70.05; H, 7.34; N, 16.39%. Calcd for $C_{15}H_{19}N_3O$: C, 70.00; H, 7.44; N, 16.33%.

3-Methallyl-5,5-dimethyl-2-(1-naphthylamino)-1-imidazolin-4-one (**10b**): yield 40%; mp 163-164 °C; ^{1}H NMR δ= 1.33 (6 H, s, 5-Me), 1.87 (3 H, s, Me), 4.30 (2 H, s, CH_2), 4.71 (1 H, br s, NH), 4.90, 4.99 (each 1 H, each d, *J*= 1.0 Hz, =CH_2), 7.00, 7.34-7.49, 7.54, 7.81, 8.01 (total 7 H, naphthyl-H). Anal. Found: C, 74.18; H, 6.93; N, 13.47%. Calcd for $C_{19}H_{21}N_3O$: C, 74.24; H, 6.89; N, 13.67%.

3-Methallyl-5,5-dimethyl-2-tosylamido-1-imidazolin-4-one (**10c**): yield 72%; mp 146-147 °C; ^{1}H NMR δ= 1.44 (6 H, s, 5-Me), 1.63 (3 H, s, -CMe=), 2.42 (3 H, s, Me), 4.05 (2 H, s, CH_2), 4.61, 4.79 (each 1 H, each s, =CH_2), 7.28, 7.81 (total 4 H, aromatic-H), 8.11 (1 H, br s, NH). Anal. Found: C, 57.36; H, 6.29; N, 12.33%. Calcd for $C_{16}H_{21}N_3O_3S$: C, 57.29; H, 6.31; N, 12.53%.

Iodocyclization of 1-Imidazolin-4-ones 7. General Procedures: To a solution of imidazolinone **7a** (0.122 g, 0.5 mmol) in DME (5 ml) was added iodine (0.381 g, 1.5 mmol) and the reaction mixture was stirred at room temperature for 1 d under argon atmosphere. The solvent was evaporated, the residue was treated with 5% sodium thiosulfate to decompose the excess of iodine and extracted with dichloromethane (3 x 15 ml). The organic layer was washed with water, dried over anhydrous magnesium sulfate, and evaporated to dryness, which was subjected to column chromatography on silica gel to afford 5-*exo* cyclization product **11a** (0.115 g, 65%) with hexane/ethyl acetate (1/1).

2-Iodomethyl-6,6-dimethyl-1-phenyl-2,3-dihydro-1*H*-imidazo[1,2-*a*]imidazol-5(6*H*)-one (**11a**): colorless prisms from hexane-benzene; mp 122-123 °C; IR (KBr) 1720 (CO), 1680 cm^{-1} (C=N); ^{1}H NMR δ= 1.40, 1.48 (each 3 H, each s, Me), 3.36 (1 H, dd, *J*= 7.7, 10.6 Hz, CH*H*I), 3.46 (1 H, dd, *J*= 2.6, 10.6 Hz, C*H*HI), 3.70 (1 H, dd, *J*= 2.9, 11.0 Hz, 3-H), 3.93 (1 H, dd, *J*= 8.1, 11.0 Hz, 3-H), 4.86 (1 H, dddd, *J*= 2.6, 2.9, 7.7, 8.1 Hz, 2-H), 7.15, 7.41, 7.54 (total 5 H, Ph); ^{13}C NMR δ= 7.4 (CH_2I), 25.1, 25.2 (6-Me), 43.0 (3-C), 61.9 (2-C), 75.3 (6-C), 119.4, 124.2, 129.7, 136.7 (Ph-C), 155.1 (7a-C), 180.7 (5-C); MS *m/z* 369 (M^+), 354 (M^+ - Me), 341 (M^+ - CO). Anal. Found: C, 45.77; H, 4.36; N, 11.30%. Calcd for $C_{14}H_{16}IN_3O$: C, 45.54; H, 4.37; N, 11.38%.

2-Iodomethyl-6,6-dimethyl-1-(1-naphthyl)-2,3-dihydro-1*H*-imidazo[1,2-*a*]imidazol-5(6*H*)-one (**11b**): colorless crystals without recrystallization; mp 154-156 °C; IR (KBr) 1720 (CO), 1670 cm^{-1} (C=N); ^{1}H NMR δ= 1.35, 1.43 (each 3 H, each s, Me), 3.16 (1 H, dd, *J*= 6.6, 10.6 Hz, CH*H*I), 3.22 (1 H, dd, *J*= 3.3, 10.6 Hz, C*H*HI), 3.77 (1 H, dd, *J*= 4.8, 11.0 Hz, 3-H), 4.18 (1 H, dd, *J*= 8.4, 11.0 Hz, 3-H), 4.68 (1 H, dddd, *J*= 3.3, 4.8, 6.6, 8.4 Hz, 2-H), 7.49-7.93 (7 H, ov, naphthyl-H); ^{13}C NMR δ= 8.2 (CH_2I), 25.1, 25.2 (6-Me), 44.3 (3-C), 64.7 (2-C), 75.1 (6-C), 122.3, 125.7, 126.4, 126.6, 126.9, 128.8, 129.1, 130.0, 131.8, 134.9 (naphthyl-C), 157.2 (7a-C), 180.9 (5-C); MS *m/z* 419 (M^+), 404 (M^+ - Me), 391 (M^+ - CO), 292 (M^+ - I). Anal. Found: C, 51.37; H, 4.36; N, 9.75%. Calcd for $C_{18}H_{18}IN_3O$: C, 51.57; H, 4.33; N, 10.02%.

2-Iodomethyl-6,6-dimethyl-1-tosyl-2,3-dihydro-1*H*-imidazo[1,2-*a*]imidazol-5(6*H*)-one (**11c**); colorless needles from ethanol; mp 143-145 °C; IR (KBr) 1740 (CO), 1660 (C=N), 1360, 1160 cm^{-1} (SO_2); 1.31, 1.43 (each 3 H, each s, 6-Me), 2.46 (3 H, s, Me), 3.52 (1 H, dd, *J*= 3.9, 11.2 Hz, 3-H), 3.52 (1 H, dd, *J*= 8.3, 10.3 Hz, CH*H*I), 3.68 (1 H, dd, *J*= 8.8, 11.2 Hz, 3-H), 3.70 (1 H, dd, *J*= 2.9, 10.3 Hz, C*H*HI), 4.59 (1 H,

dddd, *J*= 2.9, 3.9, 8.3, 8.8 Hz, 2-H), 7.36, 7.97 (total 4 H, aromatic-H); ^{13}C NMR δ= 9.1 (CH_2I), 21.7 (Me), 24.3, 24.6 (6-Me), 43.7 (3-C), 63.5 (2-H), 76.5 (6-C), 127.9, 129.9, 134.1, 145.9 (Ph-C), 153.4 (7a-C), 180.3 (5-C); MS *m/z* 447 (M^+), 432 (M^+ - Me), 419 (M^+ - CO), 383 (M^+ - SO_2). Anal. Found: C, 40.09; H, 4.07; N, 9.35%. Calcd for $C_{15}H_{18}IN_3O_3S$: C, 40.27; H, 4.06; N, 9.39%.

6-Iodo-6,6-dimethyl-8-tosyl-5,6,7,8-tetrahydroimidazo[1,2-*a*]pyrimidin-3(2*H*)-one (**12c**): colorless needles from hexane-benzene; mp 182-183 °C; IR (KBr) 1730 (CO), 1640 (C=N), 1365, 1170 cm^{-1} (SO_2); ^{1}H NMR δ= 1.24, 1.30 (each 3 H, each s, 6-Me), 2.44 (3 H, s, Me), 3.69 (1 H, ddd, *J*= 1.0, 6.6, 13.5 Hz, 5-H), 3.78 (1 H, dd, *J*= 4.6, 13.5 Hz, 5-H), 4.05 (1 H, ddd, *J*= 1.0, 7.3, 13.5 Hz, 7-H), 4.20 (1 H, dd, *J*= 3.3, 13.5 Hz, 7-H), 4.45 (1 H, dddd, *J*= 3.3, 4.6, 6.6, 7.3 Hz, 6-H), 7.31, 8.03 (total 4 H, aromatic-H); ^{13}C NMR δ= 12.1 (6-C), 21.6 (Me), 24.1, 24.7 (6-Me), 48.2 (5-C), 52.5 (7-C), 67.1 (2-C), 129.0, 129.2, 134.5, 144.7 (Ph-C), 145.2 (8a-C), 183.1 (3-C); MS *m/z* 447 (M^+), 432 (M^+ - Me), 419 (M^+ - CO), 383 (M^+ - SO_2). Anal. Found: C, 40.60; H, 4.07; N, 9.34%. Calcd for $C_{15}H_{18}IN_3O_3S$: C, 40.27; H, 4.06; N, 9.39%.

Treatment of Iodocyclization Products 11 and 12c with DBU. General Procedures: A solution of imidazoimidazole **11a** (0.185 g, 0.5 mmol) and DBU (0.149 ml, 1.0 mmol) in dry toluene (10 ml) was heated under reflux for 3 h under argon atmosphere. The solvent was evaporated, the residue was extracted with dichloromethane (3 x 10 ml), and the organic layer was dried over anhydrous magnesium sulfate. The dichloromethane was evaporated and the residue was subjected to column chromatography on silica gel to afford *exo*-methylene compound **13a** (0.117 g, 97%) with hexane/ethyl acetate (1/2).

6,6-Dimethyl-2-methylene-1-phenyl-2,3-dihydro-1*H*-imidazo[1,2-*a*]imidazol-5(6*H*)-one (**13a**): colorless plates from hexane-benzene; mp 149-151 °C; IR (KBr) 1730 (CO), 1680 cm^{-1} (C=N); ^{1}H NMR δ= 1.41 (6H, s, 6-Me), 4.25, 4.42 (each 1 H, each td, *J*= 2.2, 2.6 Hz, =CH*H*), 4.59 (2 H, t, *J*= 2.2 Hz, 3-H), 7.34-7.50 (5 H, ov, Ph); ^{13}C NMR δ= 25.0 x 2 (6-Me), 42.6 (3-C), 74.4 (6-C), 84.5 (=CH_2), 126.4, 127.8, 128.8, 133.8 (Ph-C), 145.2 (2-C), 156.2 (7a-C), 180.3 (5-C); MS *m/z* 241 (M^+), 226 (M^+ - Me), 213 (M^+ - CO). Anal. Found: C, 69.89; H, 6.28; N, 17.31%. Calcd for $C_{14}H_{15}N_3O$: C, 69.69; H, 6.27; N, 17.42%.

6,6-Dimethyl-2-methylene-1-(1-naphthyl)-2,3-dihydro-1*H*-imidazo[1,2-*a*]imidazol-5(6*H*)-one (**13b**): colorless prisms from hexane-benzene; mp 177-179 °C; IR (KBr) 1730 (CO), 1675 cm^{-1} (C=N); ^{1}H NMR δ= 1.39, 1.42 (each 3 H, each s, 6-Me), 3.89 (1 H, td, *J*= 2.2, 2.9 Hz, =CH*H*), 4.20 (1 H, ddd, *J*= 1.8, 2.2, 2.9 Hz, =C*H*H), 4.56 (1 H, ddd, *J*= 1.8, 2.2, 15.0 Hz, 3-H), 4.64 (1 H, td, *J*= 2.2, 15.0 Hz, 3-H), 7.50-7.95 (5 H, ov, naphthyl-H); ^{13}C NMR δ= 24.9, 25.1 (6-Me), 42.7 (3-C), 74.5 (6-C), 85.3 (=CH_2), 122.5, 125.9, 126.6, 126.7, 127.0, 127.1, 128.5, 129.5, 129.7, 134.8 (naphthyl-C), 146.1 (2-C), 156.7 (7a-C), 180.2 (5-C); MS *m/z* 291 (M^+), 276 (M^+ - Me), 263 (M^+ - CO). Anal. Found: C, 74.36; H, 6.06; N, 14.46%. Calcd for $C_{18}H_{17}N_3O$: C, 74.20; H, 5.88; N, 14.42%.

6,6-Dimethyl-2-methylene-1-tosyl-2,3-dihydro-1*H*-imidazo[1,2-*a*]imidazol-5(6*H*)-one (**13c**): colorless needles from hexane-benzene; mp 156-157 °C; IR (KBr) 1720 (CO), 1680 (C=N), 1360, 1170 cm^{-1} (SO_2); ^{1}H NMR δ= 1.40 (6 H, s, 6-Me), 2.45 (3 H, s, Me), 4.13 (2 H, dd, *J*= 2.0, 2.4 Hz, 3-H), 4.70 (1 H, td, *J*= 2.0, 2.9 Hz, =CH*H*), 5.68 (1 H, td, *J*= 2.4, 2.9 Hz, =C*H*H), 7.43, 7.96 (total 4 H, aromatic-H); ^{13}C NMR δ= 21.7 (Me), 24.4 x 2 (6-Me), 42.3 (3-C), 75.2 (6-C), 95.9 (=CH_2), 127.8, 129.8, 134.0, 146.1 (aromatic-C), 139.3 (2-C), 153.5 (7a-C), 179.7 (5-C); MS *m/z* 319 (M^+), 291 (M^+ - CO). Anal. Found: C, 56.39; H, 5.37; N, 12.89%. Calcd for $C_{15}H_{17}N_3O_3S$: C, 56.41; H, 5.37; N, 13.16%.

Similar treatment of 6-*endo* product **12c** with DBU gave a mixture of **14c** and **15c**, which showed a satisfactory analytical data; C, 56.66; H, 5.65; N, 13.01%. Calcd for $C_{15}H_{17}N_3O_3S$: C, 56.41; H, 5.37; N, 13.16%. The two products could not be isolated each other in pure forms, but their structures were accomplished by the spectroscopic data as follows: 2,2-dimethyl-8-tosyl-7,8-dihydroimidazo[1,2-*a*]pyrimidin-3(2*H*)-one (**14c**): ^{1}H NMR δ= 1.28 (6 H, s, 2-Me), 2.44 (3 H, s, Me), 4.43 (2 H, dd, *J*= 2.0, 3.9 Hz, 7-H), 5.33 (1 H, td, *J*= 3.9, 7.9 Hz, 6-H), 6.60 (1 H, td, *J*= 2.0, 7.9 Hz, 5-H), 7.31, 8.00 (total 4 H, aromatic-H); ^{13}C NMR δ= 21.6 (Me), 24.5 x 2 (2-Me), 44.5 (7-C), 67.6 (2-C), 104.3 (6-C), 118.1 (5-C), 128.9, 129.2, 134.4, 144.5 (aromatic-C), 145.2 (8a-C), 178.7 (3-C). 2,2-Dimethyl-8-tosyl-5,8-dihydroimidazo[1,2-*a*]-

pyrimidin-3(2*H*)-one (**15c**): ^{1}H NMR δ= 1.26 (6 H, s, 2-Me), 2.43 (3 H, s, Me), 3.95 (2 H, dd, *J*= 2.3, 3.3 Hz, 5-H), 5.18 (1 H, td, *J*= 3.3, 8.6 Hz, 6-H), 7.04 (1 H, td, *J*= 2.3, 8.6 Hz, 7-H), 7.31, 7.96 (total 4 H, aromatic-H); ^{13}C NMR = 21.7 (Me), 24.3 x 2 (2-Me), 38.8 (5-C), 67.0 (2-C), 100.3 (6-C), 122.6 (7-C), 128.9, 129.2, 134.1, 144.3 (aromatic-C), 145.5 (8a-C), 183.6 (3-C).

Iodocyclization of Imidazolinones 8 and 9 Leading to 6-endo 16 and 17 and 5-exo Cyclization Product 18c. Iodocyclization of **8** and **9** was performed similarly to the procedures mentioned above to afford the corresponding cyclization products.

(6*S**,7*R**)-6-Iodo-2,2-dimethyl-7,8-diphenyl-5,6,7,8-tetrahydroimidazo[1,2-*a*]pyrimidin-3(2*H*)-one (**16a**): colorless plates from hexane-benzene; mp 187 °C (dec.); IR (KBr) 1720 (CO), 1630 cm^{-1} (C=N); ^{1}H NMR δ= 1.43, 1.45 (each 3 H, each s, 2-Me), 3.40 (1 H, dd, *J*= 3.3, 14.5 Hz, 5-H), 3.92 (1 H, dd, *J*= 1.0, 14.5 Hz, 5-H), 4.74 (1 H, dd, *J*= 1.0, 1.3 Hz, 6-H), 5.06 (1 H, br s, 7-H), 7.14-7.44 (10 H, ov, Ph); ^{13}C NMR δ= 21.8 (6-C), 24.9, 25.7 (2-Me), 43.6 (5-C), 66.1 (2-C), 70.3 (7-C), 125.5, 126.2, 126.5, 128.8, 129.3, 129.6, 138.7, 142.4 (Ph-C), 149.1 (8a-C), 184.9 (3-C); MS *m/z* 445 (M^+), 444, 430 (M^+ - Me), 318 (M^+ - I). Anal. Found: 53.94; H,4.39; N, 9.29%. Calcd for $C_{20}H_{20}IN_3O$: C, 53.95; H, 4.53; N, 9.44%. The structure of compound **16a** was also confirmed by X-ray structure analysis.[8]

(6*S**,7*R**)-6-Iodo-2,2-dimethyl-8-(1-naphthyl)-7-phenyl-5,6,7,8-tetrahydroimidazo[1,2-*a*]pyrimidin-3(2*H*)-one (**16b**): colorless crystals without recrystallization; mp 214 °C (dec.); IR (KBr) 1730 (CO), 1630 cm^{-1} (C=N); MS *m/z* 495 (M^+), 480 (M^+ - Me), 368 (M^+ - I). Anal. Found: C, 58.12; H, 4.44; N, 8.42%. Calcd for $C_{24}H_{22}IN_3O$: C, 58.19; H, 4.48; N, 8.48%. The ^{1}H and ^{13} NMR spectra of compound **16b** showed that it existed in the $CDCl_3$ solution as a 3.3:1 mitxure of atropisomers; **major**: ^{1}H NMR δ= 1.38, 1.39 (each 3 H, each s, 2-Me), 3.79 (1 H, dd, *J*= 3.6, 14.9 Hz, 5-H), 4.09 (1 H, dd, *J*= 1.3, 14.9 Hz, 5-H), 4.66 (1 H, ddd, *J*= 1.3, 2.3, 3.6 Hz, 6-H), 4.98 (1 H, d, *J*= 2.3 Hz, 7-H), 7.08-7.90, 8.63 (total 12 H, aromatic-H); ^{13}C NMR δ= 20.2 (6-C), 25.0, 25.7 (2-Me), 44.3 (5-C), 66.3 (2-C), 70.5 (7-C), 125.2, 125.5, 125.6, 126.2, 126.5, 127.0 x 2, 128.8, 129.0, 129.1, 129.7, 135.1, 137.6, 139.7 (aromatic-C), 150.0 (8a-C), 185.1 (3-C). **Minor**: ^{1}H NMR δ= 1.34, 1.39 (each 3 H, each s, 2-Me), 3.89 (1 H, dd, *J*= 3.3, 14.5 Hz, 5-H), 4.06 (1 H, dd, *J*= 3.3, 14.5 Hz, 5-H), 4.71 (1 H, dt, *J*= 2.6, 3.3 Hz, 6-H), 5.30 (1 H, d, *J*= 2.6 Hz, 7-H), 7.08-7.90 (total 12 H, aromatic-H); ^{13}C NMR δ= 23.1 (6-C), 25.1, 25.7 (2-Me), 43.9 (5-C), 66.7 (2-C), 73.1 (7-C), 124.3, 125.4, 126.0, 126.1, 126.3, 127.2, 128.6, 128.9, 129.0, 129.6, 134.8, 139.0, 139.3 (aromatic-C), 150.0 (8a-C), 185.1 (3-C).

(6*S**,7*R**)-6-Iodo-2,2-dimethyl-7-phenyl-8-tosyl-5,6,7,8-tetrahydroimidazo[1,2-*a*]pyrimidin-3(2*H*)-one (**16c**): colorless prisms from ethanol; mp 249 °C (dec.); IR (KBr) 1730 (CO), 1630 (C=N), 1340, 1160 cm^{-1} (SO2); ^{1}H NMR (CF_3CO_2D) δ= 1.97 (6 H, s, 2-Me), 2.58 (3 H, s, Me), 3.69, 4.21 (each 1 H, each d, *J*= 14.7 Hz, 5-H), 4.93 (1 H, s, 6-H), 5.75 (1 H, s, 7-H), 7.15, 7.45-7.56, 7.92 (total 9 H, aromatic-H); ^{13}C NMR (CF_3CO_2D) δ= 15.5 (6-C), 22.6 (Me), 24.2, 25.8 (2-Me), 46.1 (5-C), 66.2 (2-C), 70.8 (7-C), 127.5, 131.4, 132.1, 132.2, 132.5, 133.3, 135.9, 153.5 (aromatic-C), 154.7 (8a-C), 177.0 (3-C); MS *m/z* 523 (M^+), 508 (M^+ - Me), 459 (M^+ - SO_2). Anal. Found: C, 48.23; H, 4.18; N, 8.02%. Calcd for $C_{21}H_{22}IN_3O_3S$: C, 48.19; H, 4.24; N, 8.03%.

(6*S**,7*R**)-6-Iodo-2,2,7-trimethyl-8-phenyl-5,6,7,8-tetrahydroimidazo[1,2-*a*]pyrimidin-3(2*H*)-one (**17a**): colorless plates from hexane-benzene; mp 172 °C (dec.); IR (KBr) 1730 (CO), 1630 cm^{-1} (C=N); ^{1}H NMR δ= 1.34, 1.35 (each 3 H, each s, 2-Me), 1.36 (3 H, d, *J*= 6.6 Hz, 7-Me), 3.90 (1 H, dd, *J*= 3.6, 14.8 Hz, 5-H), 4.01-4.11 (2 H, ov, 5- and 7-H), 4.62 (1 H, ddd, *J*= 1.0, 3.3, 3.6 Hz, 6-H), 7.25-7.46 (total 5 H, ov, Ph). Anal. Found: C, 47.43; H, 4.79; N, 10.89%. Calcd for $C_{15}H_{18}IN_3O$: C, 47.01; H, 4.73; N, 10.96%. The structure of compound **17a** was also confirmed by X-ray structure analysis.[8]

Similar reaction of imidazolinone **9c** with iodine gave two cyclization products **17c** and **18c**, which could be separated each other by column chromatography on silica gel with hexane/ethyl acetate (3/1).

(6*S**,7*R**)-6-Iodo-2,2,7-trimethyl-8-tosyl-5,6,7,8-tetrahydroimidazo[1,2-*a*]pyrimidin-3(2*H*)-one (**17c**): colorless plates from ethanol; mp 162-163 °C; IR (KBr) 1740 (CO), 1630 (C=N), 1420, 1160 cm^{-1} (SO_2); ^{1}H

NMR δ= 1.17, 1.38 (each 3 H, each s, 2-Me), 1.53 (3 H, d, *J*= 6.9 Hz, 7-Me), 2.42 (3 H, s, Me), 3.73 (1 H, dd, *J*= 3.6, 14.8 Hz, 5-H), 3.87 (1 H, dd, *J*= 1.7, 14.8 Hz, 5-H), 4.55 (1 H, ddd, *J*= 1.7, 2.0, 3.6 Hz, 6-H), 4.85 (1 H, dq, *J*= 2.0, 6.9 Hz, 7-H), 7.28, 8.11 (total 4 H, aromatic-H); ^{13}C NMR δ= 20.2 (6-C), 21.1 (7-Me), 21.7 (Me), 24.0, 25.1 (2-Me), 43.8 (5-C), 59.8 (7-C), 66.8 (2-C), 128.5, 130.1, 134.6, 144.1 (aromatic-C), 145.0 (8a-C), 184.0 (3-C); MS *m/z* 461 (M^+), 397 (M^+ - SO_2), 334 (M^+ - I), 306 (M^+ - Ts). Anal. Found: C, 41.54; H, 4.36; N, 9.00%. Calcd for $C_{16}H_{20}IN_3O_3S$: C, 41.66; H, 4.37; N, 9.11%.

(2*S**,8*R**)-2-(1-Iodoethyl)-6,6-dimethyl-1-tosyl-2,3-dihydro-1*H*-imidazo[1,2-*a*]imidazol-5(6*H*)-one (**18c**): colorless films; ^{1}H NMR δ= 1.33, 1.42 (each 3 H, each s, 2-Me), 1.87 (3 H, d, *J*= 7.3 Hz, CHI-*Me*), 2.46 (3 H, s, Me), 3.54 (2 H, d, *J*= 5.6 Hz, 2-H), 4.07 (1 H, dt, *J*= 3.3, 5.6 Hz, 6-H), 4.69 (1 H, dq, *J*= 3.3, 7.3 Hz, C*H*I-Me), 7.35, 7.98 (total 4 H, aromatic-H); ^{13}C NMR δ= 21.7 (Me), 23.9 (CHI-*Me*), 24.4, 24.5 (6-Me), 31.0 (3-C), 41.6 (*C*HI-Me), 68.6 (2-C), 76.8 (6-C), 127.9, 129.9, 134.9, 145.8 (aromatic-C), 153.1 (7a-C), 180.4 (5-C). Anal. Found: C, 41.12; H, 4.60; N, 9.68%. Calcd for $C_{16}H_{20}IN_3O_3S$: C, 41.66; H, 4.37; N, 9.11%.

Elimination of Hydrogen Iodide from the 6-endo 16 and 17c and 5-exo Cyclization Product 18c by the Treatment with DBU. A toluene solution of imidazolinone **16a** and DBU (2.0 equiv.) was heated under reflux for 1 h under argon atmosphere. Concentration, extraction with dichloromethane, and silica gel column separation gave product **19a** (97%).

2,2-Dimethyl-7,8-diphenyl-7,8-dihydroimidazo[1,2-*a*]pyrimidin-3(2*H*)-one (**19a**): colorless needles from hexane-benzene; mp 142-143 °C; IR (KBr) 1740 (CO), 1635 cm^{-1} (C=N); ^{1}H NMR δ= 1.37, 1.41 (each 3 H, each s, 2-Me), 5.24 (1 H, d, *J*= 4.6 Hz, 7-H), 5.43 (1 H, dd, *J*= 4.6, 7.9 Hz, 6-H), 6.83 (1 H, d, *J*= 7.9 Hz, 5-H), 7.10-7.35 (total 10H, Ph); ^{13}C NMR δ= 25.1, 25.3 (2-Me), 63.4 (7-C), 66.6 (2-C), 110.1 (6-C), 116.5 (5-C), 126.6, 126.7, 126.8, 128.2, 128.9, 129.1, 129.2, 140.5 (Ph-C), 148.7 (8a-C), 180.1 (3-C); MS *m/z* 317 (M^+), 302 (M^+ - Me), 289 (M^+ - CO). Anal. Found: C, 75.84; H, 6.04; N, 13.12%. Calcd for $C_{20}H_{19}N_3O$: C, 75.68; H, 6.03; N, 13.24%.

2,2-Dimethyl-8-(1-naphthyl)-7-phenyl-7,8-dihydroimidazo[1,2-*a*]pyrimidin-3(2*H*)-one (**19b**): yield 92%; colorless prisms from hexane-benzene; mp 196-197 °C; IR (KBr) 1730 (CO), 1640 cm^{-1} (C=N); MS *m/z* 367 (M^+), 352 (M^+- Me), 339 (M^+- CO). Anal. Found: C, 78.67; H, 5.80; 11.34%. Calcd for $C_{24}H_{21}N_3O$: C, 78.45; H, 5.76; N, 11.44%. This compound existed as a 3:1 mixture of atropisomers in the $CDCl_3$ solution; **major**: ^{1}H NMR δ= 1.26, 1.39 (each 3 H, each s, 2-Me), 5.05 (1 H, dd, *J*= 1.3, 4.6 Hz, 7-H), 5.49 (1 H, dd, *J*= 4.6 7.9 Hz, 6-H), 6.77 (1 H, dd, *J*= 1.3, 7.9 Hz, 5-H), 6.96-7.91 (total 10 H, aromatic-H); ^{13}C NMR δ= 25.2, 25.3 (2-Me), 63.5 (7-C), 66.6 (2-C), 109.8 (6-C), 117.1 (5-C), 121.8, 125.5, 126.1, 126.9, 127.5 x 2, 128.0, 128.5, 128.6, 128.8, 128.9, 129.3, 135.0, 140.6 (aromatic-C), 148.9 (8a-C), 180.3 (3-C). **Minor**: ^{1}H NMR δ= 1.30, 1.39 (each 3 H, each s, 2-Me), 5.39 (1 H, dd, *J*= 3.0, 7.9 Hz, 6-H), 5.50 (1 H, dd, *J*= 1.3, 3.0 Hz, 6-H), 6.96-7.91 (12 H, ov, 5-H and aromatic-H); ^{13}C NMR δ= 25.0, 25.4 (2-Me), 64.8 (7-C), 66.7 (2-C), 109.6 (6-C), 117.4 (5-C), 123.6, 124.9, 125.8, 126.1, 126.9, 127.5, 127.8, 128.2, 128.6, 128.8, 130.9, 134.2, 138.4 (aromatic-C), 148.3 (8a-C), 180.1 (3-C).

2,2-Dimethyl-7-phenyl-8-tosyl-7,8-dihydroimidazo[1,2-*a*]pyrimidin-3(2*H*)-one (**19c**): yield 73%; colorless plates from hexane-benzene; mp 146-147 °C; IR (KBr) 1740 (CO), 1630 (C=N), 1360, 1175 cm^{-1} (SO_2); ^{1}H NMR δ= 1.23, 1.34 (each 3 H, each s, 2-Me), 2.36 (3 H, s, Me), 5.52 (1 H, dd, *J*= 5.6, 7.9 Hz, 6-H), 6.05 (1 H, dd, *J*= 1.3, 5.6 Hz, 7-H), 6.68 (1 H, dd, *J*= 1.3, 7.9 Hz, 5-H), 7.11, 7.16-7.29, 7.65 (total 9 H, aromatic-H); ^{13}C NMR δ= 21.5 (Me), 24.2, 25.6 (2-Me), 58.9 (7-C), 67.7 (2-C), 110.0 (6-C), 116.6 (5-C), 126.6, 128.5, 128.7, 129.0, 129.1, 135.2, 139.1, 144.5 (aromatic-C), 144.7 (8a-C), 179.0 (3-C); MS *m/z* 395 (M^+), 331 (M^+ - SO_2). Anal. Found: C, 63.88; H, 5.30; N, 10.48%. Calcd for $C_{21}H_{21}N_3O_3S$: C, 63.78; H, 5.35; N, 10.63%.

2,2,7-Trimethyl-8-tosyl-7,8-dihydroimidazo[1,2-*a*]pyrimidin-3(2*H*)-one (**20c**): yield 89%; colorless plates from ethanol; mp 124-125 °C; IR (KBr) 1730 (CO), 1640 (C=N), 1380, 1170 cm^{-1} (SO_2); ^{1}H NMR δ=

1.06, 1.38 (each 3 H, each s, 2-Me), 1.44 (3 H, d, *J*= 6.6 Hz, 7-Me), 2.42 (3 H, s, Me), 5.12 (1 H, dq, *J*= 5.3, 6.6 Hz, 7-H), 5.42 (1 H, dd, *J*= 5.3, 7.9 Hz, 7-H), 6.56 (1 H, d, *J*= 7.9 Hz, 5-H), 7.28, 7.93 (total 4 H, aromatic-H); ^{13}C NMR δ= 21.6 (Me), 23.3 (7-Me), 24.3, 24.4 (2-Me), 52.2 (7-C), 67.6 (2-C), 111.2 (6-C), 117.0 (5-C), 128.8, 129.1, 135.6, 144.5 (aromatic-C), 144.8 (7a-C), 179.0 (3-C); MS *m/z* 333 (M^+), 318 (M^+ - Me), 290 (M^+ - HNCO), 254 (318 - SO_2). Anal. Found: C, 57.84; H, 5.79; N, 12.58%. Calcd for $C_{16}H_{19}N_3O_3S$: C, 57.64; H, 5.74; N, 12.60%.

2-*(E)*-Ethylidene-6,6-dimethyl-1-tosyl-2,3-dihydro-1*H*-imidazo[1,2-*a*]imidazol-5(6*H*)-one (**21c**): yield 72%; colorless films; ^{1}H NMR δ= 1.39 (6 H, s, 6-Me), 1.65 (3 H, d, *J*= 7.3 Hz, =CH-*Me*), 2.45 (3 H, s, Me), 4.05 (2 H, ov, 3-H), 6.16 (1 H, m, =C*H*-Me), 7.33, 7.89 (total 4 H, aromatic-H); ^{13}C NMR δ= 12.9 (=CH-*Me*), 21.7 (Me), 24.4 x 2 (6-Me), 40.3 (3-C), 75.1 (6-C), 108.1 (=*C*H-Me), 127.7, 129.7, 134.2, 145.9 (aromatic-C), 132.9 (2-C), 153.9 (8a-C), 180.0 (5-C). Anal. Found: C, 57.90; H, 6.00; N, 12.32%. Calcd for $C_{16}H_{19}N_3O_3S$: C, 57.64; H, 5.74; N, 12.60%. The configuration of the ethylidene moiety was assigned to be *E*-one by NOE measurement; irradiation of the methylene proton signal (δ= 4.05) caused an 8.4% enhancement of the methyl proton signal (δ= 1.65) of the ethylidene.

Iodocyclization of Imidazolinones 10 Leading to Imidazo[1,2-a]imidazoles 22. Iodocyclization of **10** was performed similarly to the procedures mentioned above to afford the corresponding cyclization products **22**.

2-Iodomethyl-2,6,6-trimethyl-1-phenyl-2,3-dihydro-1*H*-imidazo[1,2-*a*]imidazol-5(6*H*)-one (**22a**): colorless prisms from hexane-benzene; mp 150-151 °C; IR (KBr) 1710 (CO), 1660 cm^{-1} (C=N); ^{1}H NMR δ= 1.38, 1.40 (each 3 H, each s, 6-Me), 1.66 (3 H, s, 2-Me), 3.33, 3.37 (each 1 H, each d, *J*= 11.4 Hz, CH_2I), 3.62, 3.94 (each 1 H, each d, *J*= 11.0 Hz, 3-H), 7.33-7.45 (5 H, ov, Ph); ^{13}C NMR δ= 14.9 (CH_2I), 25.4, 25.5 (6-Me), 25.7 (2-Me), 50.7 (3-C), 69.7 (2-C), 74.7 (6-C), 128.9, 129.0, 130.1, 134.6 (Ph-C), 157.6 (7a-C), 181.3 (5-C); MS *m/z* 383 (M^+), 368 (M^+ - Me), 355 (M^+ - CO). Anal. Found: C, 46.76; H, 4.65; N, 11.05%. Calcd for $C_{15}H_{18}IN_3O$: C, 47.01; H, 4.73; N, 10.97%.

2-Iodomethyl-2,6,6-trimethyl-1-(1-naphthyl)-2,3-dihydro-1*H*-imidazo[1,2-*a*]imidazol-3(2*H*)-one (**22b**): colorless crystals without recrystallization; mp 187-188 °C; IR (KBr) 1700 (CO), 1670 cm^{-1} (C=N); MS *m/z* 433 (M^+), 405 (M^+ - CO), 306 (M^+ - I). Anal. Found: C, 52.42; H, 4.66; N, 9.58%. Calcd for $C_{19}H_{20}IN_3O$: C, 52.67; H, 4.65; N, 9.70%. This compound existed as a 3:1 mixture of atropisomers in the $CDCl_3$ solution; **major**: ^{1}H NMR δ= 1.36, 1.37 (each 3 H, each s, 6-Me), 1.44 (3 H, s, 2-Me), 3.51, 3.60 (each 1 H, each d, *J*= 10.9 Hz, CH_2I), 3.79, 4.10 (each 1 H, each d, *J*= 11.2 Hz, 3-H), 7.47-7.96 (naphthyl-H); ^{13}C NMR δ= 16.3 (CH_2I), 24.1, 24.8 (6-Me), 26.3 (2-Me), 50.7 (3-C), 70.0 (2-C), 74.4 (6-C), 123.0, 125.6, 126.5, 126.9, 128.3, 128.7, 129.8, 129.9, 131.8, 135.0 (naphthyl-C), 156.9 (7a-C), 181.0 (5-C). **Minor**: ^{1}H NMR δ= 1.36, 1.37 (each 3 H, each s, 6-Me), 1.39 (3 H, s, 2-Me), 2.98, 3.60 (each 1 H, each d, *J*= 10.9 Hz, CH_2I), 3.75, 4.10 (each 1 H, each d, *J*= 11.2 Hz, 3-H), 7.47-7.96 (naphthyl-H); ^{13}C NMR δ= 12.9 (CH_2I), 25.1, 25.5 (6-Me), 25.8 (2-Me), 51.0 (3-C), 70.7 (2-C), 74.5 (6-C), 123.3, 125.4, 126.5, 127.0, 128.6, 128.7, 129.9, 130.0, 132.0, 135.0 (naphthyl-C), 157.0 (7a-C), 181.3 (5-C).

2-Iodomethyl-2,6,6-trimethyl-1-tosyl-2,3-dihydro-1*H*-imidazolo[1,2-*a*]imidazol-5(6*H*)-one (**22c**): colorless prisms from ethanol; mp 170-171 °C; IR (KBr) 1720 (CO), 1660 (C=N), 1360, 1160 cm^{-1} (SO_2); ^{1}H NMR δ= 1.39, 1.42 (each 3 H, each s, 6-Me), 1.90 (3 H, s, 2-Me), 2.45 (3 H, s, Me), 3.41, 3.70 (each 1 H, each d, *J*= 11.0 Hz, CH_2I), 3.75, 3.88 (each 1 H, each d, *J*= 10.6 Hz, 3-H), 7.33, 8.10 (total 4 H, aromatic-H); ^{13}C NMR δ= 14.4 (CH_2I), 21.8 (Me), 24.4, 24.5 (6-Me), 25.1 (2-Me), 51.3 (3-C), 73.2 (2-C), 75.4 (6-C), 128.2, 129.5, 136.6, 145.3 (aromatic-C), 153.1 (7a-C), 180.1 (5-C); MS *m/z* 461 (M^+), 446 (M^+ - Me), 433 (M^+ - CO). Anal Found: C, 41.56; H, 4.21; N, 9.03%; Calcd for $C_{16}H_{20}IN_3O_3$: C, 41.66; H, 4.37; N, 9.11%.

Computational Procedures: All iodonium intermediates **23-26** were created and roughly optimized by using MM2 force field calculations in MacroModel (version 3.5a).[15] MO calculations were carried out with PM3 method using MOPAC program (version 6.0). All iodonium intermediates were fully optimized unless otherwise indicated.

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(*Received in Japan* 2 *October* 1995; *accepted* 25 *December* 1995)