PREPARATION OF BICYCLIC GUANIDINES BY THE IODOCYCLIZATION OF 3-ALKENYL-2-(SUBSTITUTED AMINO)-1-IMIDAZOLIN-4-ONES[1]

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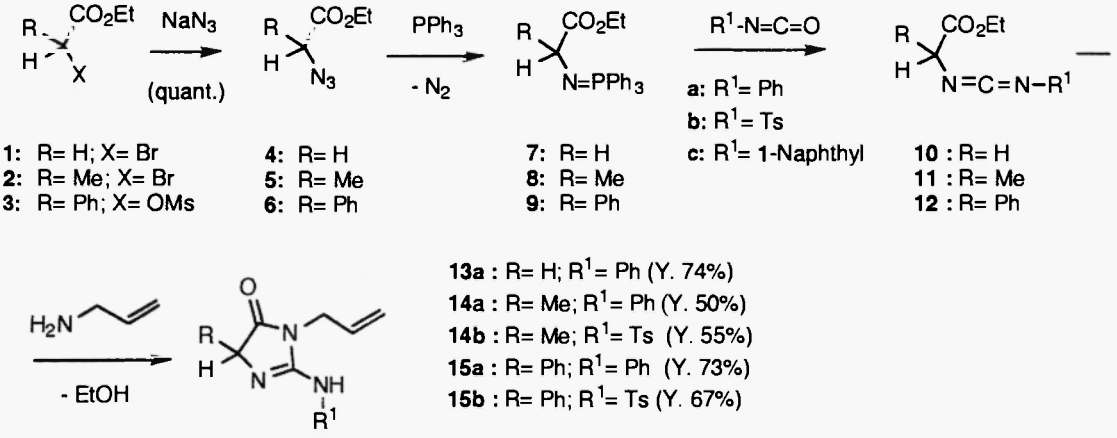
Abstract: The iodocyclization of 3-allyl-2-(substituted amino)-5-(unsubstituted)- and -5-(monosubstituted)-1-imidazolin-4-ones, which are suggested to be sensitive under such oxidative conditions, was examined; the 5-*exo* cyclization products, imidazo[1,2-*a*]imidazoles, were formed similarly to that of 5,5-dimethyl-1-imidazolin-4-ones. The scope and limitations of these cyclization were also discussed.

In previous papers,[1,2] we reported a novel synthetic route to bicyclic guanidines, imidazo[1,2-*a*]-imidazole and imidazo[1,2-*a*]pyrimidine, some derivatives of which showed a hypoglycemic activity.[3] The guanidines was formed by the iodocyclization of 3-(alk-2-enyl)-2-(substituted amino)-1-imidazolin-4-ones. The regiochemistry of the iodocyclization was predicted by the frontier electron densities for nucleophile [fr(N)] of the LUMOs of the corresponding iodonium ion intermediates. The stereochemistry of the guanidines was interpreted in terms of the stereoselective formation of the iodonium ion and its successive opening by the intramolecular nitrogen nucleophile in an S_N2 mode.[2] We report here the iodocylization of some 5-(unsubstituted)- and 5-(monosubstituted)-3-alkenyl-2-(substituted amino)-1-imidazolin-4-ones, which are suggested to be sensitive to such oxidative conditions. The scopes and limitations of these cyclizations will be also discussed.

Iodocyclizaion of 3-Allyl-5-(unsubstituted)- (13) and 3-Allyl-5-(monosubstituted)-2-(substituted amino)-1-imidazolin-4-ones (14) and (15)

The imidazolin-4-ones **13-15** were obtained according to the reported procedures in fair to good yields (Scheme 1).[2,4] The reaction of 3-allyl-2-anilino-1-imidazolin-4-one (**13a**) with iodine (3.0 equiv.) in dimethoxyethane (DME) at room temperature gave 5-*exo* cyclization product, 2-iodomethyl-1-phenyl-2,3-dihydro-1*H*-imidazo[1,2-*a*]imidazol-5(6*H*)-one (**16a**), in 47% yield. Utilizing potassium carbonate (K_2CO_3) as a scavenger of hydrogen iodide afforded an improvement of its yield up to 75%. The structure of **16a** was established on the basis of its spectroscopic data in comparison with those of the related compounds previously reported.[2,5] Similar reaction of 3-allyl-2-anilino-5-methyl- (**14a**) and 3-allyl-5-methyl-2-(tosylamino)-1-imidazolin-4-ones (**14b**) with iodine gave also 5-*exo* cyclization products **17a,b** in good yields. Imidazoimidazoles **17a,b** were obtained as mixtures of two diastereomers, respectively. The stereoselectivity of the cyclization was not so high as expected. Product **17a** was not so stable and the treatment of **17a** with DBU (2.0 equiv.) in refluxing toluene gave 6-methyl-2-methylene-1-phenyl-2,3-dihydro-1*H*-imidazo[1,2-*a*]imidazol-5(6*H*)-one (**18**) in 86% yield. Similar results were obtained in the reaction of 3-allyl-2-amlino-5-phenyl-1-imidazolin-4-ones (**15a**) with iodine; imidazoimidazole **19a** was formed as a 1:2 mixture of two diastereomers.

Scheme 1.



1: R= H; X= Br
2: R= Me; X= Br
3: R= Ph; X= OMs

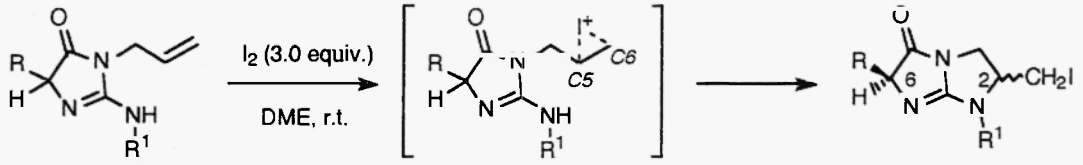
4: R= H
5: R= Me
6: R= Ph

7: R= H
8: R= Me
9: R= Ph

10 : R= H
11 : R= Me
12 : R= Ph

13a : R= H; R^1= Ph (Y. 74%)
14a : R= Me; R^1= Ph (Y. 50%)
14b : R= Me; R^1= Ts (Y. 55%)
15a : R= Ph; R^1= Ph (Y. 73%)
15b : R= Ph; R^1= Ts (Y. 67%)

Scheme 2-1.



13-15

16 : R= H
17 : R= Me
19 : R= Ph

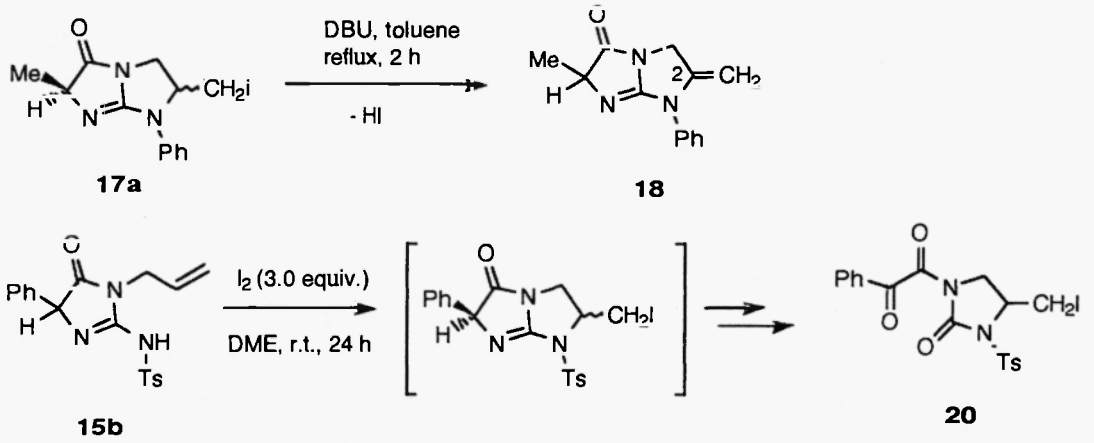
Table 1. Reaction of 3-Allyl-2-(substituted amino)-5-(unsubstituted)- (**13**) and -5-(monosubstituted)-1-imidazolin-4-ones (**14,15**) with Iodine.

Entry	Substrate	R	R^1	K_2CO_3 (equiv.)	Time (h)	Product (Yield; %)[a]	Ratio of diastereomers[b]
1	**13a**	H	Ph	none	48	**16a** (47)	
2	**13a**	H	Ph	2.0	2	**16a** (75)	
3	**14a**	Me	Ph	none	4	**17a** (51)	(1:1)
4	**14a**	Me	Ph	2.0	4	**17a** (84)	(1:1)
5	**14b**	Me	Ts	none	24	**17b** (66)	(1:1)
6	**15a**	Ph	Ph	none	24	**19a** (88)	(1:2)
7	**15b**	Ph	Ts	none	18	**20** (24)[c]	

[a] Based on the isolated products. [b] Determined by ^{1}H NMR spectra of the crude products.
[c] Unidentified products were also obtained.

The reaction of 2-tosylamino substrate **15b** with iodine gave a mixture of unidentified products together with 4-(hydroxymethyl)-1-(phenyloxalyl)-3-tosylimidazolidin-2-one (**20**) (Scheme 2). These results suggest that the iodocyclization of 5-(unsubstituted)- and 5-(monosubstituted) substrates **13-15** proceeds similarly to that of 5,5-dimethyl substrates and that some of the cyclization products are not so stable under the reaction conditions and/or purification procedures.

Scheme 2-2.

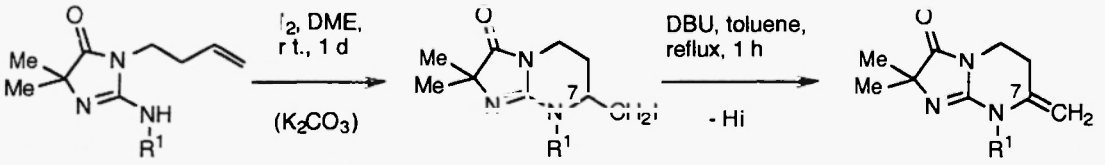


17a **18** **15b** **20**

Scopes and Limitation of the Iodocyclization of 2-Alkenyl-5,5-dimethyl-2-(substituted amino)-1-imidazolin-4-ones

Our next concern was focused on the scopes of the iodocyclization of 1-imidazolin-4-ones; 3-(but-3-enyl)-1-imidazolin-4-ones **22a-c** were also prepared by the reaction of ethyl 2-methyl-2-(*N'*-substituted carbodiimido)-propionate[2] with (but-3-enyl)amine (**21**). The similar iodocyclization of **22** gave 6-*exo* cyclization products, imidazo[1,2-*a*]pyrimidines **23**, in good yields and in the reaction of 1-imidazolin-4-ones **22a** and **22c**, utilizing K_2CO_3 as a scavenger of hydrogen iodide afforded an improvement of the yields (Scheme 3). The structures of imidazopyrimidines **23** were also confirmed by the conversion to the 7-*exo* methylene compounds **24** by the elimination of hydrogen iodide (Scheme 3). The regiochemistry of the iodocyclization was also consistent with the fr(N) obtained from the PM3 method; the values of fr(N) in the 6-*exo* cyclization were larger than those in the 7-*endo* cyclization in the corresponding iodonium ions **25** and **26** (Fig. 1).

Scheme 3.



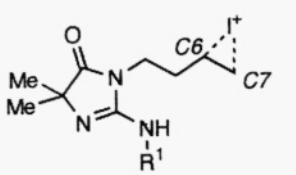
22a : R^1= Ph
22b : R^1= Ts
22c : R^1= 1-Naphthy

23a (Y. 98% with K_2CO_3)
23b (Y. 95%)
23c (Y. 89% with K_2CO_3)

24a : R^1= Ph (Y. 88%)
24b : R^1= Ts (Y. 95%)
24c : R^1= 1-Naphthyl (Y. 88%)

Fig. 1. The fr(N) values and energy levels of frontier orbitals of iodonium ions **25** and **26**.

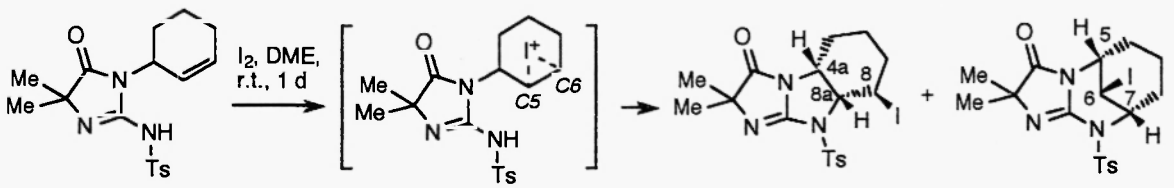
	fr(N)		Energy levels (eV)	
Ion	*C6 (exo)*	*C7 (endo)*	HOMO	LUMO
25	0.440	0.394	- 11.341	- 6.550
26	0.417	0.391	- 12.034	- 6.414



25 : R^1= Ph
26 : R^1= Ts

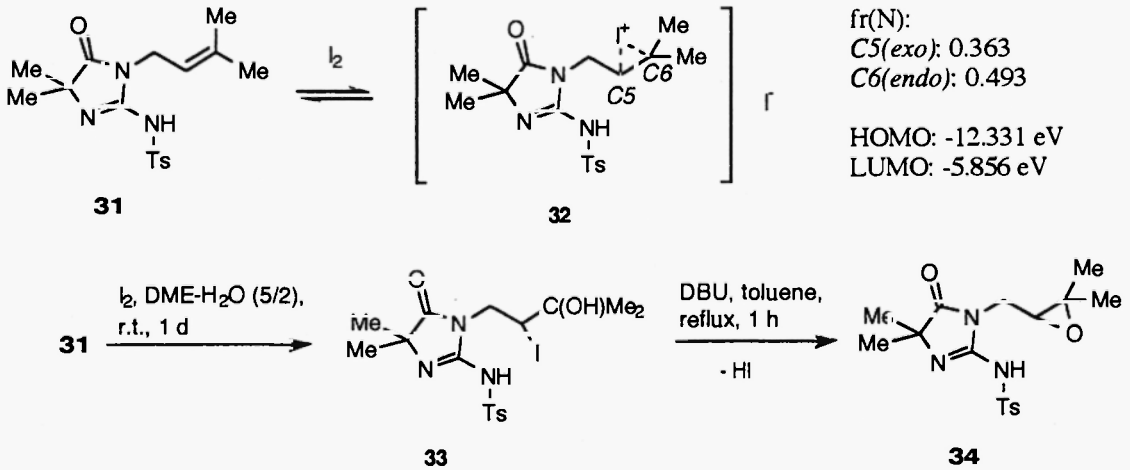
The scope of the cyclization were further examined using the 2-tosylamino substrates, which are expected to be less reactive under the iodocyclization conditions. The iodocyclization of 3-(cyclohex-2-enyl)-5,5-dimethyl-2-tosylamino-1-imidazolin-4-one (**27**) gave 5-*exo* cyclization product **28** and 6-*endo* one **29** in 21% and 77% yields, respectively. The structure of major product **29** was confirmed by X-ray crystallographic study[6] and that of minor **28** was assigned by its spectroscopic data. These suggested that the formation of the iodonium ion **30** and its opening by the intramolecular tosylamino nitrogen proceeded in a highly stereoselective manner. The similar reaction of 3-(3-methylbut-2-enyl) substrate **31** with iodine gave the unreacted **31** in recovery of 78%. The PM3 MO calculations of the iodonium ion **32** suggested the predominant formation of 6-*endo* cyclization product, although the energy difference between the frontier orbitals (ΔE= 6.475 eV) of the iodonium ion **32** was somewhat larger than those of 3-allyl substrate (ΔE= 5.720 eV)[2] and 3-(but-3-enyl) substrate **26** (ΔE= 5.620 eV). The similar reaction of **31** in the presence of water gave iodohydrin **33** in 78% yield and the regiochemistry of the addition of hypoiodide was consistent with the PM3 calculation results. The treatment of **33** with DBU gave epoxide **34** in 75% yield. These results suggest that iodonium ion **32** is expected to form and that the successive nucleophilic attack of the amino nitrogen to the ion **32** is blocked probably due to a serious steric interaction between both reaction sites.[7]

Scheme 4.



27 **30** **28** (5-*exo*) **29** (6-*endo*)

Scheme 5.



31 **32** **33** **34**

Experimental

General. For the general details of apparatuses and procedures, see the previous paper.[7] ^1H and ^{13}C NMR spectra were measured on JEOL EX-270 spectrometer (at 270 MHz for ^1H and 68 MHz for ^{13}C) in deuteriochloroform ($CDCl_3$) solution, unless otherwise stated. Assignment of the NMR spectra of products was accomplished by ^1H-^1H and ^1H-^{13}C COSY spectra. Overlapping splitting patterns in ^1H NMR spectra are indicated as ov. Ethyl azidoacetate (**4**) was obtained quantitatively by the reaction of ethyl bromoacetate with sodium azide (2.0 equiv.) in 20%-aqueous methanol at r.t. for 1 d; colorless oil, IR cm^{-1}: 2100 (N_3), 1740 (CO); ^1H NMR δ= 1.30 (3 H, t, *J*= 6.7 Hz, OCH_2CH_3), 3.85 (2 H, s, -CH_2-), 4.24 (2 H, q, *J*= 6.7 Hz, OCH_2CH_3). Ethyl 2-azidopropionate (**5**): colorless oil; IR cm^{-1}: 2110 (N_3), 1740 (CO); ^1H NMR δ= 1.21-1.50 (6 H, ov, OCH_2CH_3 and >CH-CH_3), 3.76 (1 H, q, *J*= 7.0 Hz, >CH-CH_3), 4.05 (2 H, q, *J*= 6.8 Hz, OCH_2CH_3). Ethyl 2-azido-2-phenylacetate (**6**): colorless oil; IR cm^{-1}: 2100 (N_3), 1740 (CO); ^1H NMR δ= 1.29 (3 H, t, *J*= 7.0 Hz, OCH_2CH_3), 4.20 (2 H, q, *J*= 7.0 Hz, OCH_2CH_3), 5.12 (1 H, s, >CH-Ph), 7.64 (5 H, ov, Ph). (But-3-enyl)amine (**21**), (cyclohex-2-enyl)amine, (3-methylbut-2-enyl)amine were generated *in situ* by the treatment of the corresponding hydrocholorides[8,9] with an excess of triethylamine, respectively.

Preparation of 1-Imidazolin-4-ones 13, 14, 15, 22, 27, and 31. General Procedures: To a solution of azide **4** (0.129 g, 1.0 mmol) in dry dioxane (5 ml) heated at 50 °C under nitrogen atmosphere was added triphenylphosphine (0.262 g, 1.0 mmol) in dioxane (3 ml) and immediately nitrogen was extruded. The reaction mixture was stirred at the same temperature for 4 h and cooled down to room temperature. Phenyl isocyanate (0.108 ml, 1.0 mmol) was added and stirred for 1 h. Allylamine (0.075 ml, 1.0 mmol) was added to the reaction mixture and stirred at room temperature for 24 h. The solvent was evaporated to dryness, which was extracted with dichloromethane (3 x 15 ml). The dichloromethane was evaporated and the residue was subjected to column chromatography on silica gel [hexane-ethyl acetate (2/1)] to give imidazolinone **13a** (0.159 g, 74%). Similarly, other 1-imidazolin-4-ones **14**, **15**, **22**, **27**, and **31** were prepared and their structures were fully confirmed by the analytical and spectroscopic data. The selected data are summarized as follows:

3-Allyl-2-anilino-1-imidazolin-4-one (**13a**): colorless needles (hexane-benzene); mp 68-70 °C; ^1H NMR δ= 3.92 (2 H, s, 5-H), 4.31 (2 H, d, *J*= 5.6 Hz, >N-CH_2-), 4.62 (1 H, br s, NH), 5.23 (1 H, d, *J*= 10.2 Hz, =CHH), 5.31 (1 H, d, *J*= 17.2 Hz, =CHH), 5.96 (1 H, m, -CH=), 6.95-7.33 (5 H, ov, Ph). Anal. Found: C, 66.79; H, 6.02; N, 19.31%. Calcd. for $C_{12}H_{13}N_3O$: C, 66.95; H, 6.09; N, 19.52%.

3-Allyl-2-anilino-5-methyl-1-imidazolin-4-one (**14a**): colorless viscous oil; IR cm^{-1}: 3330 (NH), 1730 (CO), 1670 (C=N); ^1H NMR δ= 1.35 (3 H, d, *J*= 6.9 Hz, 5-Me), 3.97 (1 H, q, *J*= 6.9 Hz, 5-H), 4.23 (2 H, d, *J*= 5.6 Hz, >N-CH_2-), 4.94 (1 H, br s, NH), 5.20 (1 H, dd, *J*= 9.6, 1.0 Hz, =CHH), 5.23 (1 H, dd, *J*= 16.2, 1.0 Hz, =CHH), 5.92 (1 H, m, -CH=), 6.98, 7.03, 7.30 (total 5 H, Ph); ^{13}C NMR δ= 18.5 (4-Me), 41.5 (>N-CH_2-), 53.6 (5-C), 117.5 (=CH_2), 122.7, 123.5, 129.8, 148.0 (Ph-C), 131.8 (-CH=), 149.4 (2-C), 174.5 (4-C). This compound did not give satisfactory analytical data (Found: C, 67.64; H, 6.55; N, 17.75%. Calcd for $C_{13}H_{15}N_3O$: C, 68.10; H, 6.59; N, 18.33%).

3-Allyl-5-methyl-2-tosylamino-1-imidazolin-4-one (**14b**): colorless prisms (hexane-benzene); mp 92-93 °C; ^1H NMR δ= 1.49 (3 H, d, *J*= 6.9 Hz, 5-Me), 2.42 (3 H, s, Me), 4.12 (2 H, d, *J*= 5.9 Hz, >N-CH_2-), 4.18 (1 H, q, *J*= 6.9 Hz, 5-H), 5.15 (1 H, dd, *J*= 16.2, 1.0 Hz, =CHH), 5.17 (1 H, dd, *J*= 8.6, 1.0 Hz, =CHH), 5.74 (1 H, m, -CH=), 7.28 (2 H, br d, *J*= 8.6 Hz, aromatic-H), 7.70 (1 H, br s, NH), 7.80 (2 H, d, *J*= 8.3 Hz, aromatic-H). Anal. Found: C, 54.99; H, 5.40; N, 13.56%. Calcd. for $C_{14}H_{17}N_3O_3S$: C, 54.72; H, 5.58; N, 13.68%.

3-Allyl-2-anilino-5-phenyl-1-imidazolin-4-one (**15a**): colorless prisms (hexane-benzene); mp 128-129 °C; ^1H NMR δ= 4.32 (2H, d, *J*= 5.3 Hz, >N-CH_2-), 4.98 (1 H, s, 5-H), 5.06 (1 H, br s, NH), 5.22 (1 H, d, *J*= 10.2 Hz, =CHH), 5.30 (1 H, d, *J*= 17.2 Hz, =CHH), 5.96 (1 H, m, -CH=), 7.02-7.42 (10 H, ov, Ph). Anal. Found: C, 74.52; H, 5.92; N, 14.38%. Calcd. for $C_{18}H_{17}N_3O$: C, 74.20; H, 5.88; N, 14.42%.

3-Allyl-5-phenyl-2-tosylamino-1-imidazolin-4-one (**15b**): colorless prisms (MeOH); mp 168-170 °C; ^1H NMR δ= 2.44 (3 H, s, Me), 4.16 (2 H, d, *J*= 7.0 Hz, >N-CH_2-), 5.13 (1 H, s, 5-H), 5.14 (1 H, dtd, *J*= 7.6, 1.3, 1.0 Hz, =CHH), 5.17 (1 H, dd, *J*= 14.2, 1.0 Hz, =CHH), 5.74 (1 H, m, -CH=), 7.26-7.43, 7.84 (total 9

H, aromatic-H), 7.98 (1 H, br s, NH). Anal. Found: C, 61.59; H, 5.05; N, 11.42%. Calcd. for $C_{19}H_{19}N_3O_3S$: C, 61.77; H, 5.18; N, 11.38%.

2-Anilino-3-(but-3-enyl)-5,5-dimethyl-1-imidazolin-4-one (**22a**): yield 54%; colorless prisms (hexane); mp 90 °C; ^{1}H NMR δ= 1.34 (6 H, s, 5-Me$_2$), 2.52 (2 H, q, *J*= 6.9 Hz, -C*H*$_2$-CH=), 3.74 (2 H, t, *J*= 6.9 Hz, >N-CH$_2$-), 4.65 (1 H, br, NH), 5.05 (1 H, d, *J*= 9.9 Hz, =C*H*H), 5.10 (1 H, d, *J*= 16.2 Hz, =CH*H*), 5.84 (1 H, ddt, *J*= 16.2, 9.9, 6.9 Hz, -C*H*=), 6.96, 7.04, 7.32 (total 5 H, Ph). Anal. Found: C, 69.92; H, 7.47; N, 16.20%. Calcd. for $C_{15}H_{19}N_3O$: C, 70.00; H, 7.44; N, 16.33%.

3-(But-3-enyl)-5,5-dimethyl-2-tosylamino-1-imidazolin-4-one (**22b**): yield 83%; colorless needles (EtOH); mp 115-116 °C; ^{1}H NMR δ=1.40 (6 H, s, 5-Me$_2$), 2.30 (2 H, q, *J*= 6.8 Hz, -C*H*$_2$-CH=), 2.43 (3 H, s, Me), 3.60 (2 H, t, *J*= 6.8 Hz, >N-CH$_2$-), 4.80 (1 H, dd, *J*= 19.0, 2.0 Hz, =C*H*H), 4.83 (1 H, dd, *J*= 10.3, 2.0 Hz, =CH*H*), 5.57 (1 H, ddt, *J*= 19.0, 10.3, 6.8 Hz, -CH=), 7.30, 7.84 (each 2 H, each d, *J*= 8.3 Hz, aromatic-H), 7.98 (1 H, br s, NH). Anal. Found: C, 57.30; H, 6.28; N, 12.51%. Calcd. for $C_{16}H_{21}N_3O_3S$: C, 57.29; H, 6.31; N, 12.53%.

3-(But-3-enyl)-5,5-dimethyl-2-(1-naphthyl)amino-1-imidazolin-4-one (**22c**): yield 40%; colorless plates (hexane-benzene); mp 158-159 °C; ^{1}H NMR δ= 1.29 (6 H, s, 5-Me$_2$), 2.63 (2 H, q, *J*= 6.9 Hz, -C*H*$_2$-CH=), 3.88 (2 H, t, *J*= 6.9 Hz, >N-CH$_2$-), 4.58 (1 H, br s, NH), 5.11 (1 H, dd, *J*= 9.9, 1.7 Hz, =C*H*H), 5.18 (1 H, dd, *J*= 17.2, 1.7 Hz, =CH*H*), 7.01, 7.37-7.48, 7.57, 7.82, 8.03 (total 7 H, naphthyl-H). Anal. Found: C, 74.10; H, 6.66; N, 13.90%. Calcd. for $C_{19}H_{21}N_3O$: C, 74.24; H, 6.89; N, 13.67%.n

3-(Cyclohex-2-enyl)-5,5-dimethyl-2-tosylamido-1-imidazolin-4-one (**27**): yield 60%; colorless needles (propan-2-ol); mp 164-165 °C; ^{1}H NMR δ= 1.41 (6 H, s, 5-Me$_2$), 1.58-2.18 (6 H, ov, -CH$_2$-), 2.42 (3 H, s, Me), 4.74 (1 H, m, >N-CH<), 5.38 (2 H, ov, -C*H*=C*H*-), 7.29, 7.82 (each 2 H, each d, *J*= 8.2 Hz, aromatic-H), 7.93 (1 H, br s, NH). Anal. Found: C, 59.79; H, 6.51; N, 11.50%. Calcd. for $C_{18}H_{23}N_3O_3S$: C, 59.81; H, 6.41; N, 11.62%.

5,5-Dimethyl-3-(3-methylbut-2-enyl)-2-(tosylamino)-1-imidazolin-4-one (**31**): yield 51%; colorless needles (hexane-benzene); mp 111-112 °C; ^{1}H NMR δ= 1.42 (6 H, s, 5-Me$_2$), 1.63, 1.66 (each 3 H, each s, =CMe$_2$), 2.42 (3 H, s, Me), 4.07 (2 H, d, *J*= 7.3 Hz, >N-CH$_2$-) 5.09 (1 H, t, *J*= 7.3 Hz, -CH=), 7.29, 7.82 (each 2 H, each d, *J*= 8.3 Hz, aromatic-H), 7.93 (1 H, br s, NH). Anal. Found: C, 58.35; H, 6.62; N, 11.90%. Calcd. for $C_{17}H_{23}N_3O_3S$: C, 58.43; H, 6.63; N, 12.02%.

Iodocyclization of 1-Imidazolin-4-ones 13a, 14, 15, 22, 27 and 31. General Procedures: To a solution of imidazolinone **13a** (0.0431 g, 0.2 mmol) and K_2CO_3 (0.0553 g, 0.4 mmol) in DME (2 ml) was added iodine (0.152 g, 0.6 mmol) and the reaction mixture was stirred at room temperature for 2 h. The solvent was evaporated, the residue was treated with 5% sodium thiosulfate to decompose the excess of iodine, and extracted with ethyl acetate (3 x 10 ml). The organic layer was washed with water, dried over anhydrous magnesium sulfate, and evaporated to dryness. The residue was subjected to column chromatography on silica gel [hexane-ethyl acetate (1/1)] to afford 5-*exo* cyclization product **16a** (0.0512 g, 75%).

2-Iodomethyl-1-phenyl-2,3-dihydro-1*H*-imidazo[1,2-*a*]imidazol-5(6*H*)-one (**16a**): colorless plates (hexane-benzene); mp 152-154 °C; IR cm^{-1}: 1730 (CO), 1650 (C=N); ^{1}H NMR δ= 3.33 (1 H, dd, *J*= 10.6, 8.6 Hz, -C*H*HI), 3.48 (1 H, dd, *J*= 10.6, 2.3 Hz, -CH*H*I), 3.75 (1 H, dd, *J*= 11.2, 3.3 Hz, 3-H), 3.97 (1 H, dd, *J*= 11.2, 8.6 Hz, 3-H), 4.37, 4.48 (each 1 H, each d, *J*= 21.4 Hz, 6-H), 4.92 (1 H, m, 2-H), 7.13-7.58 (5 H, ov, Ph); ^{13}C NMR δ= 6.7 (-CH$_2$I), 43.1 (3-C), 62.5 (2-C), 64.1 (6-C), 119.0, 124.3, 129.6, 136.5 (Ph-C), 158.3 (7a-C), 175.5 (5-C). Anal. Found: C, 41.97; H, 3.52; N, 12.10%. Calcd. for $C_{12}H_{12}IN_3O$: C, 42.25; H, 3.55; N, 12.32%.

Similarly, the iodocyclization of **14a** gave 5-*exo* cyclization product **17a** (in 84% yield) as a mixture of two diastereomers (1.1 : 1), which could not be separated completely. Product **17a** was not so stable and gradually decomposed. The treatment of **17a** with DBU (2.0 equiv.) in refluxing toluene for 2 h followed by usual work-up gave 2-*exo* methylene **18** in 86% yield.

2-Iodomethyl-6-methyl-1-phenyl-2,3-dihydro-1*H*-imidazo[1,2-*a*]midazol-5(6*H*)-one (**17a**): pale yellow viscous oil; IR cm^{-1}: 1730 (CO); 1660 (C=N). Compound **17a** did not give satisfactory analytical data owing to

its instability (Found: C, 44.60; H, 4.41; N, 11.70%. Calcd for $C_{13}H_{14}IN_3O$: C, 43.94; H, 3.94; N, 11.83%). Product **17a** consisted of two diastereomers and their ^1H and ^{13}C NMR spectra are shown. **Major:** ^1H NMR δ= 1.45 (3 H, d, *J*= 7.6 Hz, 6-Me), 3.28-3.49 (2 H, ov , -CH_2I), 3.68 (1 H, dd, 5-H, *J*= 11.2, 3.7 Hz, 5-H), 3.98 (1 H, dd, *J*= 11.2, 3.0 Hz, 5-H), 4.49 (1 H, q, *J*= 7.6 Hz, 6-H), 4.89 (1 H, m, 2-H), 7.14, 7.39, 7.58 (total 5 H, Ph); ^{13}C NMR δ= 6.8 (CH_2I), 17.6 (6-Me), 42.9 (3-C), 62.1 (2-C), 70.1 (6-C), 119.2, 124.2, 129.5, 136.5 (Ph-C), 156.7 (7a-C), 178.4 (5-C). **Minor:** ^1H NMR δ= 1.52 (3 H, d, *J*= 7.3 Hz, 6-Me), 3.28-3.49 (2 H, ov, -CH_2I), 3.71 (1 H, dd, *J*= 11.2, 3.7 Hz, 3-H), 3.94 (1 H, dd, *J*= 11.2, 2.6 Hz, 3-H), 4.45 (1 H, q, *J*= 7.3 Hz, 6-H), 7.23, 7.42, 7.55 (total 5 H, Ph); ^{13}C NMR δ= 7.2 (CH_2I), 17.6 (6-Me), 42.9 (3-C), 61.9 (2-C), 70.4 (6-C), 118.9, 124.0, 129.5, 136.4 (Ph-C), 156.7 (7a-C), 178.4 (5-C).

6-Methyl-2-methylene-1-phenyl-2,3-dihydro-1*H*-imidazo[1,2-*a*]imidazol-5(6*H*)-one (**18**): pale yellow prisms (hexane-benzene); mp 114-115 °C; IR cm^{-1}: 1730 (CO), 1640 (C=N); ^1H NMR δ= 1.46 (3 H, d, *J*= 7.3 Hz, 6-Me), 4.27 (1 H, dt, *J*= 2.6, 2.0 Hz, =C*H*H), 4.40-4.47 (3 H, ov, 5-H and =CH*H*), 4.42 (1 H, q, *J*= 7.3 Hz, 6-H), 7.33-7.53 (5 H, ov, Ph); ^{13}C NMR δ= 17.5 (6-Me), 42.7 (3-C), 69.6 (6-C), 84.8 (=CH_2), 126.5, 128.0, 129.8, 133.7 (Ph-C), 145.3 (2-C), 157.9 (7a-C), 177.9 (5-C). Anal. Found: C, 68.91; H, 5.73; N, 18.31%. Calcd. for $C_{13}H_{13}N_3O$: C, 68.70; H, 5.77; N, 18.49%.

2-Iodomethyl-6-methyl-1-tosyl-2,3-dihydro-1*H*-imidazo[1,2-*a*]imidazol-5(6*H*)-one (**17b**): colorless needles (hexane-propan-2-ol); mp 146-148 °C; IR cm^{-1}: 1730 (CO), 1660 (C=N), 1360, 1160 (SO_2). Anal. Found: 38.75; H, 3.76; N, 9.62%. Calcd. for $C_{14}H_{16}INO_3S$: C, 38.81; H, 3.72; N, 9.70%. Compound **17b** consisted of two diastereomers (1.1 : 1) and their ^1H and ^{13}C spectral data are shown. **Major**: ^1H NMR δ= 1.47 (3 H, d, *J*= 7.6 Hz, 6-Me), 2.47 (3 H, s, Me), 3.50 (1 H, dd, *J*= 10.9, 4.3 Hz, 3-H), 2.51 (1 H, dd, *J*= 10.6, 3.9 Hz, -C*H*HI), 3.69 (1 H, dd, *J*= 10.9, 5.6 Hz, 5-H), 3.74 (1 H, dd, *J*= 10.6, 3.3 Hz, -CH*H*I), 4.43 (1 H, q, *J*= 7.6 Hz, 6-H), 4.69 (1 H, m, 2-H), 7.38, 7.99 (each 2 H, each d, *J*= 8.2 Hz, aromatic-H); ^{13}C NMR δ= 8.8 (-CH_2I), 17.0 (6-Me), 21.7 (Me), 43.8 (3-C), 63.6 (2-C), 71.4 (6-C), 127.9, 130.1, 134.8, 145.9 (aromatic-C), 154.8 (7a-C), 178.1 (5-C). **Minor**: ^1H NMR δ= 1.38 (3 H, d, *J*= 7.6 Hz, 6-Me), 2.47 (3 H, s, Me), 3.42-3.54 (2 H, ov, 3-H and -C*H*HI), 3.60-3.78 (2 H, ov, 3-H and -CH*H*I), 4.43 (1 H, q, *J*= 7.6 Hz, 6-H), 7.38, 7.99 (each 2 H, each d, *J*= 8.2 Hz, aromatic-H); ^{13}C NMR δ= 8.8 (-CH_2I), 17.0 (6-Me), 21.8 (Me), 43.8 (3-C), 63.6 (2-C), 71.4 (6-C), 127.9, 130.1, 134.8, 145.9 (aromatic-C), 154.8 (7a-C), 178.1 (5-C).

2-Iodomethyl-1,6-diphenyl-2,3-dihydro-1*H*-imidazo[1,2-*a*]imidazol-5(6*H*)-one (**19a**): colorless crystals; mp 74-76 °C (without recrystallization due to its thermal instability); IR cm^{-1}: 1730 (CO), 1660 (C=N). Anal. Found: C, 52.23; H, 4.10; N, 9.65%. Calcd. for $C_{18}H_{16}IN_3O$: C, 51.82; H, 3.87; N, 10.07%. Compound **19a** consisted of two diastereomers (1.1 : 1) and their ^1H and ^{13}C NMR spectral data are shown. **Major**: ^1H NMR δ= 3.37-3.54 (2 H, ov, -CH_2I), 3.78 (1 H, dd, *J*= 11.2, 3.3 Hz, 3-H), 3.92 (1 H, dd, *J*= 11.2, 8.3 Hz, 3-H), 4.93 (1 H, m, 2-H), 5.54 (1 H, s, 6-H), 7.14-7.69 (10 H, ov, Ph); ^{13}C NMR δ= 6.8 (-CH_2I), 43.3 (3-C), 62.5 (2-C), 77.1 (6-C), 119.2, 124.3, 126.8, 127.9, 128.6, 129.7, 1366.2, 136.5 (Ph-C), 157.6 (7a-C), 175.8 (5-C). **Minor**: ^1H NMR δ= 3.33-3.49 (2 H, ov, -CH_2I), 3.70 (1 H, dd, *J*= 11.2, 3.0 Hz, 3-H), 4.00 (1 H, dd, *J*= 11.2, 8.2 Hz, 3-H), 4.93 (1 H, m, 2-H), 5.48 (1 H, s, 6-H), 7.14-7.69 (10 H, ov, Ph); ^{13}C NMR δ= 7.4 (-CH_2I), 43.2 (5-C), 61.9 (6-C), 77.5 (2-C), 119.4, 124.4, 126.9, 128.0, 128.5, 129.7, 136.4, 136.7 (Ph-C), 157.8 (7a-C), 175.6 (5-C).

4-Iodomethyl-1-phenyloxalyl-3-tosylimidazolidin-2-one (**20**): This compound was obtained as colorless needles (hexane-benzene) and revealed to be a 1:1 molecular complex of product **20** and benzene; mp 105-106 °C; IR cm^{-1}: 1750 (CO), 1680 (C=N); ^1H NMR δ= 2.44 (3 H, s, Me), 3.55-3.61 (1 H, dd, *J*= 11.6, 6.5 Hz, -C*H*HI), 3.64 (1 H, dd, *J*= 11.9, 3.0 Hz, 4-H), 3.83 (1 H, dd, *J*= 11.6, 3.3 Hz, -CH*H*I), 4.05 (1 H, dd, *J*= 11.9, 9.2 Hz, 4-H), 4.55 (1 H, m, 5-H), 7.26-7.89 (9 H, ov, aromatic-H), 7.36 (6 H, s, benzene-H); ^{13}C NMR δ= 9.2 (CH_2I), 21.7 (Me), 45.4 (4-C), 54.1 (5-C), 128.3-134.8, 146.1 (aromatic-C), 128.7 (benzene-C), 149.4 (2-C), 166.1 (-CO-*C*O-N<), 187.3 (Ph-*C*O-). Anal. Found: C, 50.41; H, 3.89; N, 4.53%. Calcd. for $C_{19}H_{17}IN_2O_5S \cdot C_6H_6$: C, 50.86; H, 3.93; N, 4.74%.

7-Iodomethyl-2,2-dimethyl-8-phenyl-5,6,7,8-tetrahydroimidazo[1,2-*a*]pyrimidin-3(2*H*)-one (**23a**): colorless prisms (hexane-benzene); mp 134-135 °C; IR cm^{-1}: 1725 (CO), 1630 (C=N); ^1H NMR δ= 1.28, 1.33 (each 3 H, each s, 2-Me_2), 2.19, 2.26 (each 1 H, each m, 6-H), 3.13 (1 H, dd, *J*= 10.9, 10.6 Hz, -C*H*HI), 3.36 (1 H, dd, *J*= 10.6, 3.6 Hz, -CH*H*I), 3.57 (1 H, ddd, *J*= 13.2, 11.9, 4.6 Hz, 5-H), 3.84 (1 H, ddd, *J*= 13.2, 5.6, 3.3 Hz, 5-H), 4.09 (1 H, m, 7-H), 7.25-7.50 (5 H, ov, Ph); ^{13}C NMR δ= 4.0 (CH_2I), 24.5 (6-C), 24.9, 25.0 (2-Me_2), 34.3 (5-C), 58.2 (7-C), 65.6 (2-C), 127.0, 127.3, 129.8, 140.4 (Ph-C), 150.2 (8a-C), 184.4 (3-C); MS *m/z:* 383 (M^+), 368 (M^+ - Me), 355 (M^+ - CO), 256 (M^+ - I). Anal. Found: C, 47.10; H, 4.69; N, 10.84%. Calcd. for $C_{15}H_{18}IN_3O$: C, 47.01; H, 4.73; N, 10.97%

7-Iodomethyl-2,2-dimethyl-8-tosylimino-5,6,7,8-tetrahydroimidazo[1,2-*a*]pyrimidin-3(2*H*)-one (**23b**): colorless prisms (EtOH); mp 165-166 °C; IR cm^{-1}: 1720 (CO), 1620 (C=N), 1360, 1160 (SO_2); ^1H NMR δ= 1.11, 1.32 (each 3 H, each s, 2-Me_2), 1.95 (1 H, m, 6-H), 2.43 (3 H, s, Me), 2.66 (1 H, m, 6-H), 3.17 (1 H, dd, *J*= 11.6, 10.6 Hz, -C*H*HI), 3.31 (1 H, td, *J*= 13.2, 4.6 Hz, 5-H), 3.54-3.66 (2 H, ov, 5-H and -CH*H*I), 4.87 (1 H, m, 7-H), 7.29, 7.98 (each 2 H, each d, *J*= 8.3 Hz, aromatic-H); ^{13}C NMR δ= 3.4 (CH_2I), 21.6 (Me), 24.1 (6-C), 24.2, 24.4 (2-Me_2), 54.4 (7-C), 66.6 (2-C), 128.8, 129.2, 135.4, 145.1 (aromatic-C), 145.5 (8a-C), 183.7 (3-C); MS *m/z:* 461 (M^+), 446 (M^+ - Me), 397 (M^+ - SO_2). Anal. Found: 41.62; H, 4.35; N, 9.11%. Calcd. for $C_{16}H_{20}IN_3O_3S$: C, 41.66; H, 4.37; N, 9.11%.

7-Iodomethyl-2,2-dimethyl-8-(1-naphthyl)-5,6,7,8-tetrahydroimidazo[1,2-*a*]pyrimidin-3(2*H*)-one (**23c**): colorless crystals; mp 171-173 °C (without recrystallization); IR cm^{-1}: 1720 (CO), 1630 (C=N); MS *m/z:* 433 (M^+), 418 (M^+ - Me), 405 (M^+ - CO), 306 (M^+ - I). Anal. Found: C, 52.50; H, 4.65; N, 9.56%. Calcd. for $C_{19}H_{20}IN_3O$: C, 52.67; H, 4.65; N, 9.70%. The ^1H and ^{13}C NMR spectra of compound **23c** showed that it existed in the $CDCl_3$ solution as a 2:1 mixture of atropisomers. **Major:** ^1H NMR δ= 1.19, 1.31 (each 3 H, each s, 2-Me_2), 2.46-2.56 (1 H, ov, 6-H), 2.67-2.78 (1 H, ov, 6-H), 3.25 (1 H, dd, *J*= 10.2, 8.3 Hz, -C*H*HI), 3.48 (1 H, dd, *J*= 10.2, 2.6 Hz, -CH*H*I), 3.57-3.68 (1 H, ov, 5-H), 3.82-4.00 (2 H, ov, 5- and 7-H), 7.45-7.94 (7 H, ov, naphthyl-H); ^{13}C NMR δ= 4.3 (CH_2I), 24.6 (6-C), 24.9, 25.0 (2-Me_2), 34.3 (5-C), 57.3 (7-C), 65.6 (2-C), 121.2, 125.7, 126.4 x 2, 127.1, 128.4, 129.1, 129.6, 135.3, 135.5 (naphthyl-C), 150.4 (8a-C), 184.6 (3-C). **Minor:** ^1H NMR δ= 1.22, 1.23 (each 3 H, each s, 2-Me_2), 2.46-2.56 (1 H, ov, 6-H), 2.67-2.78 (1 H, ov, 6-H), 3.07 (1 H, dd, *J*= 10.2, 3.3 Hz, -C*H*HI), 3.17 (1 H, dd, *J*= 10.2, 7.9 Hz, -CH*H*I), 3.57-3.68 (1 H, ov, 5-H), 3.82-4.00 (2 H, ov, 5-H), 4.15 (1 H, m, 7-H), 7.45-7.94 (7 H, ov, naphthyl-H); ^{13}C NMR δ= 4.5 (CH_2I), 24.7 (6-C), 25.1, 25.6 (2-Me_2), 34.4 (5-C), 60.6 (7-C), 65.9 (2-C), 123.2, 125.6, 126.1 x 2, 126.7, 128.8, 129.3, 131.1, 134.7, 137.4 (naphthyl-C), 150.4 (8a-C), 184.4 (3-C).

2,2-Dimethyl-7-methylene-8-phenyl-5,6,7,8-tetrahydroimidazo[1,2-*a*]pyrimidin-3(2*H*)-one (**24a**): colorless needles (EtOH); mp 138-140 °C; IR cm^{-1}: 1730 (CO), 1630 (C=N); ^1H NMR δ= 1.30 (6 H, s, 2-Me_2), 2.78 (2 H, t, *J*= 6.3 Hz, 6-H), 3.70 (2 H, t, *J*= 6.3 Hz, 5-H), 3.79 (1 H, s, =C*H*H), 4.16 (1 H, s, =CH*H*), 7.16-7.68 (5 H, ov, Ph); ^{13}C NMR δ= 24.7 (2-Me_2), 28.9 (6-C), 37.2 (5-C), 66.6 (2-C), 93.2 (=CH_2), 128.2, 129.0, 129.8, 138.4 (Ph-C), 142.7 (7-C), 150.1 (8a-C), 184.1 (3-C). Anal. Found: C, 67.83; H, 6.82; N, 15.74%. Calcd. for $C_{15}H_{17}N_3O \cdot I/2H_2O$: C, 68.18; H, 6.81: N, 15.90%.

2,2-Dimethyl-7-methylene-8-tosyl-5,6,7,8-tetrahydroimidazo[1,2-*a*]pyrimidin-3(2*H*)-one (**24b**): colorless plates (EtOH); mp 182-183 °C; IR cm^{-1}: 1730 (CO), 1620 (C=N), 1360, 1170 (SO_2); ^1H NMR δ= 1.22 (6 H, s, 2-Me_2), 2.41 (2 H, t, *J*= 6.2 Hz, 6-H), 2.43 (3 H, s, Me), 3.47 (2 H, t, *J*= 6.2 Hz, 5-H), 5.27 (1 H, d, *J*= 1.1 Hz, =C*H*H), 5.45 (1 H, d, *J*= 1.1 Hz, =CH*H*), 7.29, 7.92 (each 2 H, each d, *J*= 8.4 Hz, aromatic-H); ^{13}C NMR δ= 22.0 (Me), 24.7 (2-Me_2), 29.2 (6-C), 39.8 (5-C), 67.4 (2-C), 113.7 (=CH_2), 129.1, 129.7, 135.9, 145.6 (aromatic-C), 137.2 (7-C), 147.3 (8a-C), 184.1 (3-C); MS *m/z:* 333 (M^+), 318 (M^+ - Me), 269 (M^+ - SO_2). Anal. Found: C, 57.68; H, 5.76; N, 12.59%. Calcd. for $C_{16}H_{19}N_3O_3S$: C, 57.64; H, 5.74; N, 12.60%.

2,2-Dimethyl-7-methylene-8-(1-naphthyl)-5,6,7,8-tetrahydroimidazo[1,2-*a*]pyrimidin-3(2*H*)-one (**24c**): colorless plates (hexane-benzene); mp 147-148 °C; IR cm^{-1}: 1730 (CO), 1620 (C=N); ^1H NMR δ= 1.21, 1.29 (each 3 H, each s, 2-Me_2), 2.86 (1 H, ddd, *J*= 15.2, 6.6, 5.9 Hz, 6-H), 2.91 (1 H, ddd, *J*= 15.2, 6.6, 5.9 Hz, 6-H), 3.57 (1 H, s, =C*H*H), 3.78 (1 H, ddd, *J*= 13.5, 6.6, 5.9 Hz, 5-H), 3.84 (1 H, ddd, *J*= 13.5, 6.6, 5.9

Hz, 5-H), 4.09 (1 H, s, =CH*H*), 7.46-7.91 (7 H, ov, naphthyl-H); ^{13}C NMR δ= 24.6, 24.9 (2-Me$_2$), 28.9 (6-C), 37.4 (5-C), 66.8 (2-C), 93.3 (=CH$_2$), 122.3, 126.0, 126.3, 126.8, 127.8, 128.7, 129.3, 129.8, 134.6, 135.0 (naphthyl-C), 142.2 (6-C), 150.1 (8a-C), 184.1 (3-C); MS *m/z:* 305 (M^+), 290 (M^+ - Me), 277 (M^+ - CO). Anal. Found: C, 74.75; H, 6.38; N, 13.75%. Calcd. for $C_{19}H_{19}N_3O$: C, 74.73; H, 6.27; 13.76%.

(4a*R**,8*R**,8a*S**)-8-Iodo-2,2-dimethyl-9-tosyl-5,6,7,8,8a,9-hexahydro-4a*H*-imidazo[1,2-*a*]benzimidazol-3(2*H*)-one (**28**): colorless plates (propan-2-ol); mp 143-144 °C; IR cm^{-1}: 1730 (CO); 1660 (C=N), 1370, 1170 (SO$_2$); ^{1}H NMR δ= 1.27, 1.42 (each 3 H, each s, 2-Me$_2$), 2.46 (3 H, s, Me), 1.68-2.43 (total 6 H, ov, 5-, 6- and 7-H), 2.46 (3 H, s, Me), 4.18 (1 H, dd, *J*= 7.6, 6.3 Hz, 8-H), 4.38 (1 H, m, 4a-H), 5.34 (1H, m, 8a-H), 7.37, 7.93 (each 2 H, each d, *J*= 8.6 Hz, aromatic-H); ^{13}C NMR δ= 18.8 (8-C), 21.7 (Me), 24.3, 24.5 (2-Me$_2$), 26.0, 26.8, 29.4 (5-, 6-, and 7-C), 48.7 (8a-C), 69.5 (4a-C), 76.1 (2-C), 128.5, 129.9, 132.2, 146.1 (aromaic-C), 144.3 (9a-C), 180.6 (3-C). Anal. Found: C, 44.30; H, 4.57; N, 8.54%. Calcd. for $C_{18}H_{22}IN_3O_3S$: C, 44.36; H, 4.55; N, 8.62%.

(5*R**,6*R**,7*S**)-6-Iodo-2,2-dimethyl-8-tosyl-5,6,7,8-tetrahydro-5,7-trimethyleneimidazo[1,2-*a*]-pyrimidin-3(2*H*)-one (**29**): colorless prisms (hexane-benzene); mp 176-177 °C; IR cm^{-1}: 1730 (CO), 1620 (C=N), 1380, 1170 (SO$_2$); ^{1}H NMR δ= 1.21, 1.28 (each 3 H, each s, 2-Me), 1.03-2.67 (6 H, ov, 9-, 10-, and 11-H), 2.43 (3 H, ov, Me), 4.17 (1 H, d, *J*= 1.3 Hz, 5-H), 4.21 (1 H, dd, *J*= 2.0, 1.3 Hz, 6-H), 4.82 (1 H, d, *J*= 2.0 Hz, 7-H), 7.27, 7.99 (each 2 H, each d, *J*= 8.3 Hz, aromatic-H); ^{13}C NMR δ= 15.5 (6-C), 19.8 (10-C), 21.6 (Me), 24.0, 24.5 (2-Me$_2$), 24.4, 25.9 (9- and 11-C), 50.0, 56.2 (5- and 7-C), 67.3 (2-C), 128.8, 129.1, 135.4, 145.0 (aromatic-C), 146.7 (8a-C), 182.3 (3-C); MS *m/z:* 488 (M^+ + H), 487 (M^+), 423 (M^+ - SO$_2$), 332 (M^+ - Ts). Anal. Found: C, 44.46; H, 4.58; N, 8.58%. Calcd. for $C_{18}H_{22}IN_3O_3S$: C, 44.36; H, 4.55; N, 8.62%. The structure of compound **29** was also confirmed by X-ray structure analysis.[6]

3-(Hydroxy-2-iodo-3-methylbutyl)-5,5-dimethyl-2-(tosylamino)-1-imidazolin-4-one (**33**): colorless prisms (hexane-benzene); mp 141-142 °C; IR cm^{-1}: 3400 (OH), 3320 (NH), 1750 (CO), 1620 (C=N), 1390, 1140 (SO$_2$); ^{1}H NMR δ= 1.39, 1.41 (each 3 H, each s, -C(OH)*Me*$_2$)), 1.46, 1.49 (each 3 H, each s, 5-Me$_2$), 2.04 (1 H, s, OH), 2.42 (3 H, s, Me), 3.73 (1 H, dd, *J*= 14.5, 4.3 Hz, >N-CH$_2$-), 4.11 (1 H, dd, *J*= 14.5, 10.9 Hz, >N-CH$_2$-), 4.62 (1 H, dd, *J*= 10.9, 4.3 Hz, -CHI-), 7.32, 7.84 (each 2 H, each d, *J*= 8.3 Hz, aromatic-H), 8.03 (1 H, br s, NH); ^{13}C NMR δ= 21.5 (Me), 24.6, 24.7 (C(OH)*Me*$_2$), 27.7, 28.0 (5-Me), 43.3, 45.9 (>N-*C*H$_2$-*C*HI-), 60.4 (5-C), 71.7 (*C*(OH)Me$_2$), 126.2, 129.5, 139.1, 143.3 (aromatic-C), 154.3 (2-C), 175.7 (4-C); MS *m/z:* 493 (M^+), 476 (M^+ - OH), 435 (M^+ - Me$_2$CO), 366 (M^+ - I). Anal. Found: C, 41.37; H, 4.88; N, 8.47%. Calcd. for $C_{17}H_{24}IN_3O_4S$: C, 41.39: H, 4.90; N, 8.52%.

5,5-Dimethyl-3-(3-methyl-2,3-epoxybutyl)-2-tosylamino-1-imidazolin-4-one (**34**): colorless prisms (hexane-benzene); mp 141-142 °C; IR cm^{-1}: 1750 (CO), 1630 (C=N), 1380, 1130 (SO$_2$); ^{1}H NMR δ= 1.22, 1.30 (each 3 H, each s, >CMe$_2$), 1.44, 1.46 (each 3 H, each s, 5-Me$_2$), 2.42 (3 H, s, Me), 2.89 (1 H, dd, *J*= 5.6, 5.9 Hz, -CH<), 3.58 (1 H, dd, *J*= 14.5, 5.6 Hz, >N-C*H*H-), 3.77 (1 H, dd, *J*= 14.5, 5.9 Hz, >N-CH*H*-), 7.28, 7.78 (each 2 H, each d, *J*= 7.3 Hz, aromatic-H), 8.15 (1 H, br s, NH); ^{13}C NMR δ= 18.8 x 2 (>C*Me*$_2$), 21.4 (Me), 24.1, 24.5 (5-Me$_2$), 38.5 (>N-CH$_2$-), 59.2, 59.7 (bridgehead carbons of the epoxide), 60.4 (5-C), 126.1, 129.4, 139.1, 143.2 (aromatic-C), 154.5 (2-C), 175.9 (4-C); MS *m/z:* 365 (M^+), 210 (M^+ - Ts). Anal. Found: C, 55.91; H, 6.34; N, 11.54%. Calcd. for $C_{17}H_{23}N_3O_4S$: C, 55.87; H, 6.32; N, 11.50%.

Computational Procedures: All iodonium ion intermediates **25**, **26**, and **32** were created and roughly optimized by using MM2 force field calculations in MacroModel (version 3.5a).[10] MO calculations were carried out with PM3 method[11] using MOPAC program (version 6.0).[12] All iodonium ion intermediates were fully optimized unless otherwise indicated.

References and Notes

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Received May 17, 1996