Pergamon

Tetrahedron, Vol. 52, No. 19, pp. 6581-6590, 1996

0040-4020/96 $15.00 + 0.00

S0040-4020(96)00314-6

IODOCYCLIZATION OF 3-ALKYNYL- AND 3-ALLENYL-2-(SUBSTITUTED AMINO)-1-IMIDAZOLIN-4-ONES[1]

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Abstract: The iodocyclization of 3-alkynyl-2-(substituted amino)-1-imidazolin-4-ones proceeded in regio- and stereo-selective manner to give bicyclic guanidines, imidazo[1,2-*a*]imidazole and/or imidazo[1,2-*a*]pyrimidine. The regiochemistry and reactivity of the cyclization were interpretable by the PM3 MO calculations of the iodonium ion intermediates.

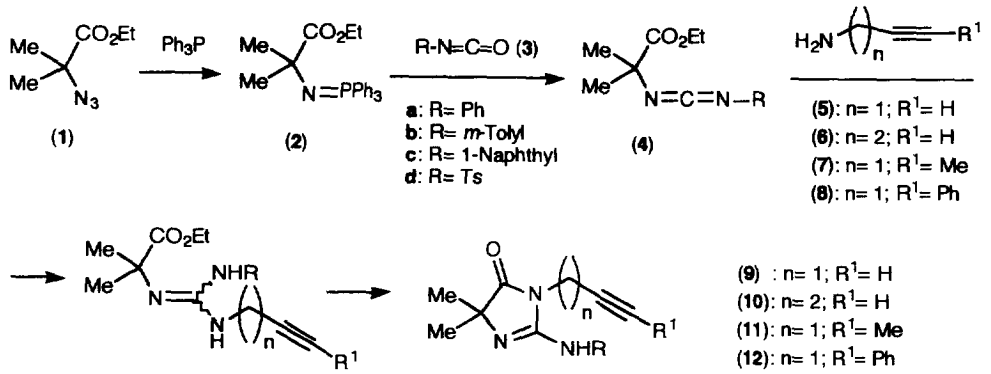
In the previous paper, we described the facile preparation of imidazo[1,2-*a*]imidazoles and/or imidazo[1,2-*a*]pyrimidines by the iodocyclization of 3-(alk-2-enyl)-2-(substituted amino)-1-imidazolin-4-ones.[1] The regiochemistry of the cyclization depended on the kind of the substituents of alkenyl moieties and was interpretable on the basis of the PM3 molecular orbital (MO) calculations of the iodonium ion intermediates. Although many examples of regio- and stereo-selective alkene-iodocyclization and its development to key synthetic step of naturally occurring products were found in the literatures,[2] alkyne-iodocyclization reactions were relatively rare.[3] Our attention, therefore, was concentrated on the iodocyclization of 3-alkynyl-2-(substituted amino)-1-imidazolin-4-ones. The alkyne-iodocyclization reaction was less reactive and in some cases the addition of iodine to the triple bond was competitive to each other. Similar cyclization of 3-allenyl substrates was also examined. These cyclizations proceeded regio- and stereo-selectively and the regioselectivity would be discussed using the PM3 MO calculation data of the iodonium ions.

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

Preparation of the starting materials, 1-imidazolin-4-ones, was similar to that of the corresponding alkenyl substrates. Ethyl 2-methyl-2-(*N'*-substituted)carbodiimidopropionates (**4**), formed *in situ* by the reaction of iminophosphorane **2** with isocyanates **3**, were allowed to react with alkynylamines **5-8** to give imidazolinones **9-12** in fair to moderate yields (Scheme 1 and see Experimental section).

The results of iodocyclization of imidazolinones **9** and **10** (R^1= H) are summarized in Table 1. The reaction of 2-anilino-3-(prop-2-ynyl)-1-imidazolinone (**9a**) with iodine (3.0 equiv.) in dimethoxyethane (DME) at room temperature for 1 day gave 5-*exo* cyclization product, 2-(iodomethylene)-6,6-dimethyl-1-phenyl-2,3-dihydro-1*H*-imidazo[1,2-*a*]imidazol-5(6*H*)-one (**13a**), in 77% yield. The structure of **13a** was accomplished on the basis of the analytical and spectroscopic data; its ^{1}H and ^{13}C NMR spectra were quite similar to those of 6,6-dimethyl-2-methylene-1-phenyl-2,3-dihydro-1*H*-imidazo[1,2-*a*]imidazol-5(6*H*)-one (**14a**)[1] except for the iodomethylene moiety. In its ^{13}C NMR spectrum the olefin carbon attached to iodine atom was shielded by the iodine atom and observed at δ= 47.2 (the *exo* methylene carbon of **14a** was observed at δ= 84.5). The configuration of the *exo*-methylene moiety of **13a** was deduced to be *E*-configuration from the nuclear Overhauser effect (NOE) measurements; the irradiation of phenyl protons caused 6.4% enhancement of the olefin proton signal at δ= 5.28. However, no NOEs were observed between the olefin proton (δ= 5.28) and the methylene protons at the 3-position (δ= 4.34). The iodocyclization of 2-(1-naphthylamino) substrate **9c** gave 5-

Scheme 1



Scheme 2

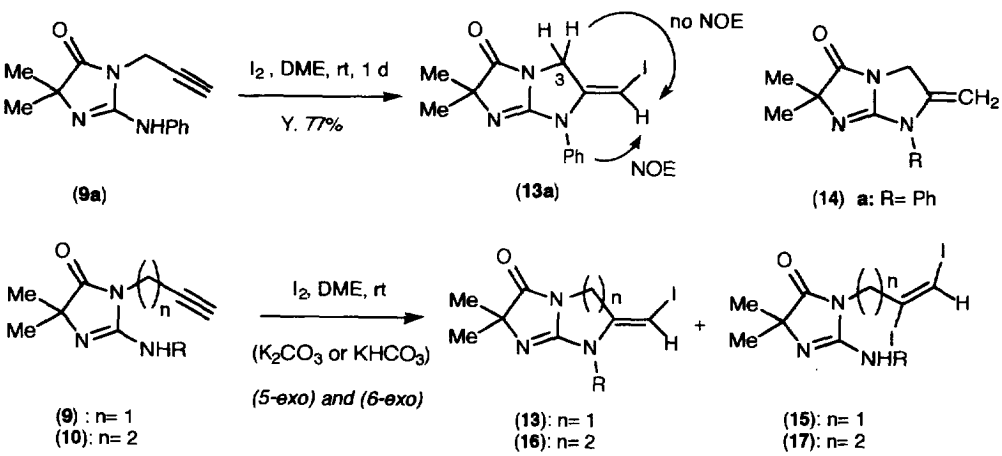


Table 1. Reaction of 3-Alkynyl-5,5-dimethyl-2-(substituted amino)-1-imidazolin-4-ones **9** and **10** with Iodine.

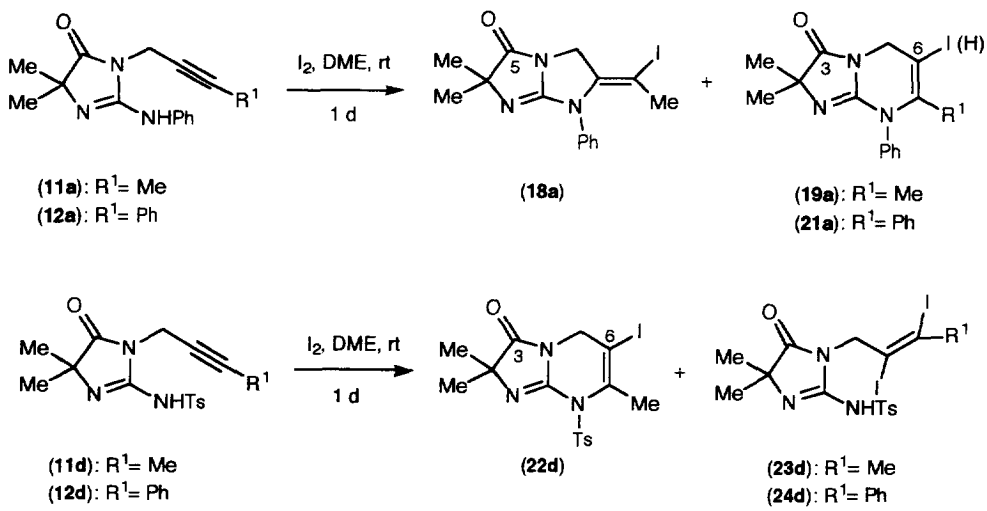
Entry	Substrate	R	Base (equiv.)	Time (h)	Products (Yield; %)[a]
1	**9a**	Ph	none	24	**13a** (77)
2	**9a**	Ph	K_2CO_3 (1.0)	6	**13a** (81)
3	**9a**	Ph	$KHCO_3$ (2.0)	3	**13a** (74)
4	**9c**	1-Naphthyl	none	24	**13c** (87) **15c** (3)
5	**9d**	Ts	none	24	**13d** (54) **15d** (26)
6	**10a**	Ph	none	24	**16a** (52)
7	**10a**	Ph	K_2CO_3 (1.0)	8	**16a** (89)
8	**10b**	*m*-Tolyl	none	24	**16b** (80)
9	**10b**	*m*-Tolyl	K_2CO_3 (1.0)	24	**16b** (81)
10	**10d**	Ts	none	24	**16d** (67) **17d** (8)

[a] Based on the isolated products.

exo cyclization product **13c** together with a trace of diiodide **15c**. On the other hand, the iodocyclization of 2-tosylamino substrate **9d** gave 5-*exo* cyclization product **13d** and diiodide **15d** in a ratio of 2:1 (Scheme 2). Similar reaction of 2-anilino- **10a** and 2-(*m*-toluidino)-3-(but-3-ynyl)-1-imidazolinone **10b** with iodine gave 6-*exo* cyclization products **16a** and **16b**. In the former case, utilizing potassium carbonate as a scavenger of hydrogen iodide resulted in an improvement of the yield. The reaction of 3-(but-3-ynyl)-2-tosylamino-1-imidazolinone **10d** with iodine afforded the corresponding 6-*exo* cyclization product **16d** and diiodide **17d** in 67 and 8% yields, respectively. The configuration of the *exo*-methylene moieties in the 6-*exo* cyclization products **16** was assumed to be *(E)*-configuration from the chemical shifts of the olefin proton in their ^{1}H NMR spectra and the possible reaction pathway. The reaction pathway to the 5-*exo* and 6-*exo* cyclization products was explained by the formation of three membered cyclic iodonium ion intermediates and the successive ring opening by the intramolecular attack of nitrogen atoms. The regiochemistry of the cyclization and the formation of diiodides **15** and **17** are discussed later using the results of PM3 MO calculations of the corresponding iodonium ion intermediates.

Our concern was focused on the reaction of 3-(but-2-ynyl)- **11** and 3-(3-phenylprop-2-ynyl)imidazolinones **12** with iodine; when a solution of 2-anilino-3-(but-2-ynyl) substrate **11a** and iodine in DME was allowed to stir at room temperature for 1 d, 5-*exo* cyclization product **18a** and 6-*endo* one **19a** were formed in 14 and 77% yields, respectively. The structures of the products **18a** and **19a** were also established by their analytical and spectroscopic data in comparison with those of the related systems such as **13** and 1-substituted imidazoimidazolones **14**[1] and 2,2-dimethyl-8-tosyl-7,8-dihydroimidazo[1,2-*a*]pyrimidin-3(2*H*)-one (**20**).[1] Especially, the chemical shifts of the carbonyl carbon were useful for the assignment of the 5-*exo* cyclization

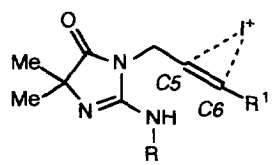
Scheme 3



product **18a**, imidazoimidazolone (δ= 180.1) , and the 6-*endo* one **19a**, imidazopyrimidinone (δ= 183.7). The configuration of the *exo*-methylene moiety in **18a** was tentatively assigned to be *(E)*-configuration. The similar reaction of 2-anilino substrate **12a** with iodine gave the 6-*endo* product **21a** (δ_{CO}= 183.8) in 86% yield. Considerably different results were obtained in the reaction of 2-tosylamino substrates **11d** and **12d** with iodine; mixtures of unidentified products, probably due to the decomposition of the starting materials, were formed along with the 6-*endo* cyclization product **22d** (δ_{CO}= 183.0) and diiodides **23d** and **24d** (Scheme 3).

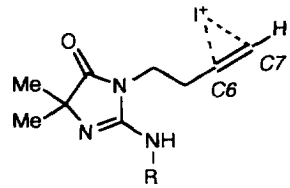
In order to discuss the regiochemistry of the iodocyclization, the PM3 MO calculations of the corresponding iodonium ions **25-28** were examined on the assumption that this iodocyclization would proceed *via* the iodonium

Table 2. Energy Levels of the Frontier Orbitals of the Iodonium Ions **25-28** and Their Frontier Electron Densities for Nucleophile [fr(N)] in the *exo*- and *endo*-Cyclizations.



(**25**): R^1= H
(**27**): R^1= Me
(**28**): R^1= Ph

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



(**26a**): R= Ph
(**26d**): R= Ts

Entry	Iodonium ion	R	R^1	Energy Level (eV) HOMO	LUMO	Frontier Electron Density for Nucleophile [fr(N)] *C5-exo*	*C6-endo*
1	**25a**	Ph	H	- 11.962	- 6.722	0.442	0.277
2	**25d**	Ts	H	- 12.131	- 6.204	0.453	0.204
3	**27a**	Ph	Me	- 11.925	- 6.495	0.341	0.385
4	**27d**	Ts	Me	- 12.067	- 6.020	0.307	0.345
5	**28a**	Ph	Ph	- 11.189	- 6.895	0.022	0.741
6	**28d**	Ts	Ph	- 12.334	- 6.453	0.025	0.740
						C6-exo	*C7-endo*
7	**26a**	Ph	H	- 11.121	- 6.577	0.450	0.253
8	**26d**	Ts	H	- 11.825	- 6.500	0.451	0.239

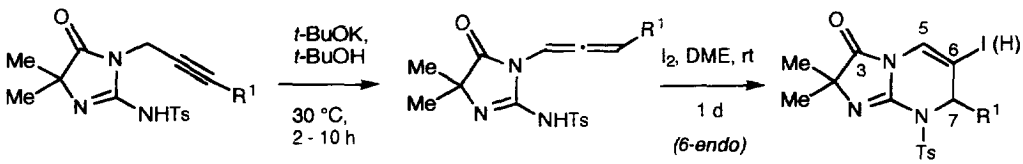
ion intermediates. The frontier electron densities for nucleophile [fr(N)] in the 5-*exo* and 6-*endo* cyclizations of the LUMOs of the ions **25**, **27**, and **28**, and those in the 6-*exo* and 7-*endo* cyclizations of the ion **26** are demonstrated in Table 2. Both iodonium ions **25a,d** from **9a** and **9d** have lager fr(N) at the C-5 position than those at the C-6 position. A similar tendency of the *exo*-predominance is observed in the iodonium ions **26a,d** from **10a** and **10d**. This suggests that the 5-*exo* and 6-*exo* cyclizations are predominant in the ions **25** and **26**, respectively. The iodonium ions **27a,d** and **28a,d** have larger fr(N) values at the C-6 position than those at the C-5 position. This also suggests that the 6-*endo* cyclizations are predominant in the ions **27** and **28**. The regiochemistry of these iodocyclizations is consist with the results of the PM3 MO calculation data of the corresponding iodonium ion intermediates. The formation of diiodides **15d**, **23d**, and **24d** could be explained also by the calculation data: the frontier electron densities for electrophile [fr(E)] of the HOMOs of the tosylamino-type iodonium ions **25d**, **27d**, and **28d** are located to the three nitrogen atoms and C-2 atom. On the other hand, the fr(E) of the anilino-type iodonium ions **25a**, **27a**, and **28a** are located to the N-1, anilino nitrogen atom, C-2 atom and anilino phenyl.[4] This suggests that the both amino nitrogens of the anilino- and tosylamino-moieties in these ions could participate in the iodocyclization. A considerable difference between the HOMO and LUMO levels in the tosylamino-type ion such as **28d** seems to be a reason for the exclusive formation of diiodide **24d**.

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

Although isomerization of propargyl group to allenyl one with a strong base has been well-known, little attention has been paid to the iodocyclizations of allene systems so far.[5] In the course of this study, we examined the iodocyclization of 3-allenyl-1-imidazolinones. The isomerization of 3-propargyl substrates **9** to 3-allenyl derivatives were examined using potassium *t*-butoxide (*t*-BuOK) according to the reported methods;[6] only 5,5-dimethyl-3-(propa-1,2-dienyl)-2-tosylamino-1-imidazolin-4-one (**29d**) could be isolated in a pure form, when the tosylamino substrate **9d** was treated with *t*-BuOK in *t*-BuOH at 30 °C. Similarly, 3-(3-phenylpropa-1,2-dienyl)-5,5-dimethyl-2-tosylamino-1-imidazolin-4-one (**30d**) was formed from imidazolinone **12d** (see Experimental section). The reaction of allenyl substrates **29d** and **30d** with iodine gave the 6-*endo* cyclization

products **31d** and **32d** in 46 and 66% yields, respectively (Scheme 4). The structures of the products **31d** and **32d** were established on the basis of the analytical and spectroscopic data. In the ^{1}H-^{13}C COSY spectra of **31d** and **32d** as well as their DEPT measurements, the signals assignable to iodomethyl carbon (-CH_2I) and/or iodomethylene one (-CHI-) could not be observed.[7] Their ^{1}H and ^{13}C spectral patterns were similar to those of the 7,8-dihydroimidazo[1,2-*a*]pyrimidine-3(2*H*)-ones **33**[1] except for the 6-H and 7-C.

Scheme 4



(**9d**) : R^1= H
(**12d**): R^1= Ph

(**29d**): R^1= H
(**30d**): R^1= Ph

(**31d**): R^1= H
(**32d**): R^1= Ph
(**33**): R^1= H, Me, Ph;
without (I)-atom

Conclusion

The iodocyclization of 3-alkynyl-2-(substituted amino)-1-imidazolin-4-ones gave bicyclic guanidines, imidazo[1,2-*a*]imidazole and imidazo[1,2-*a*]pyrimidine, in regio- and stereo-selective manners. The regiochemistry of the cyclization was explainable using the fr(N) values of the corresponding iodonium ion intermediates calculated by PM3 MO method. The 3-allenyl-2-tosylamino substrate **30d**, obtained from the corresponding 3-alkynyl substrate **12d**, showed a higher reactivity than **12d** under the iodocyclization conditions. Further application of the iodocyclization to the selective preparation of nitrogen containing heterocycles are in progress in our laboratory.

Experimental

General. For general details of apparatuses and procedures, see the previous paper.[1] ^{1}H and ^{13}C NMR spectra were measured on a JEOL EX-270 spectrometer (at 270 MHz for ^{1}H and 68 MHz for ^{13}C) in deuteriochloroform solution, unless otherwise stated. Overlapping splitting patterns in ^{1}H NMR spectra are indicated as ov. Assignment of the NMR spectra of the products was accomplished by ^{1}H-^{1}H and ^{1}H-^{13}C COSY spectra. Alkynylamines **5-8** were generated by the reaction of the corresponding hydrochlorides[8,9] with an excess of triethylamine *in situ*.

Preparation of 1-Imidazolin-4-ones 9-12. General Procedures: To a solution of azide **1** (1.2 mmol) in dry dioxane (5 ml) heated at 80 °C under argon atmosphere was added triphenylphosphine (1.0 mmol) in dry dioxane 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 (**3a**; 1.0 mmol) was added and stirred for 1 h. Propargylamine hydrochloride[8] (1.5 mmol) and triethylamine (2.0 mmol) were added to the mixture and stirred at room temperature for 13 h. Evaporation of the solvent, extraction with dichloromethane, and usual column separation [silica gel, hexane-ethyl acetate (4/1)] gave imidazolinone **9a** in 36% yield. Similarly, other 1-imidazolin-4-ones **9-12** were obtained and their structures were fully confirmed by the analytical and spectroscopic data. The selected data are summarized as follows:

2-Anilino-5,5-dimethyl-3-(prop-2-ynyl)-1-imidazolin-4-one (**9a**): yield 36%; mp 158-160 °C; ^{1}H NMR δ=1.34 (6 H, s, 5-Me), 2.23 (1 H, t, *J*= 2.6 Hz, ≡CH), 4.42 (2 H, d, *J*= 2.6 Hz, >NCH_2-), 4.84 (1 H, br s, NH), 6.89, 7.06, 7.32 (total 5 H, Ph). Anal. Found: C, 69.53; H, 6.25; N, 17.18%. Calcd for $C_{14}H_{15}N_3O$: C, 69.69; H, 6.27; N, 17.42%.

5,5-Dimethyl-2-(1-naphthyl)amino-3-(prop-2-ynyl)-1-imidazolin-4-one (**9c**): yield 37%; mp 161-162 °C; ^{1}H NMR δ= 1.33 (6 H, s, 5-Me), 2.31 (1 H, t, *J*= 2.3 Hz, ≡CH), 4.54 (2 H, d, *J*= 2.3 Hz, >NCH$_2$-), 4.73 (1 H, br s, NH), 7.03, 7.37-7.49, 7.57, 7.82, 8.11 (total 7 H, aromatic-H). Anal. Found: C, 74.25; H, 5.91; N, 14.40%. Calcd for $C_{18}H_{17}N_3O$: C, 74.20; H, 5.88; N, 14.42%.

5,5-Dimethyl-3-(prop-2-ynyl)-2-tosylamino-1-imidazolin-4-one (**9d**): yield 87%; mp 185-186 °C; ^{1}H NMR δ= 1.45 (6 H, s, 5-Me), 2.15 (1 H, t, *J*= 2.9 Hz, ≡CH), 2.42 (3 H, s, Me), 4.29 (2 H, d, *J*= 2.9 Hz, >NCH$_2$-), 7.30, 7.86 (total 4 H, Ph), 8.06 (1 H, br s, NH). Anal. Found: 56.63; H, 5.43; N, 12.94%. Calcd for $C_{15}H_{17}N_3O_3S$: C, 56.42; H, 5.37; N, 13.16%.

2-Anilino-3-(but-3-ynyl)-5,5-dimethyl-1-imidazolin-4-one (**10a**): yield 42%; mp 131-132 °C; ^{1}H NMR δ= 1.38 (6 H, s, 5-Me), 1.98 (1 H, t, *J*= 2.6 Hz, ≡CH), 2.64 (2 H, td, *J*= 6.9, 2.6 Hz, -C*H*$_2$-C≡CH), 3.84 (2 H, t, *J*= 6.9 Hz, >NCH$_2$-), 4.73 (1 H, br s, NH), 6.96, 7.06, 7.32 (total 5 H, Ph). Anal. Found: C, 70.66; H, 6.78; N, 16.37%. Calcd for $C_{15}H_{17}N_3O$: C, 70.56; H, 6.71; N, 16.46%.

3-(But-3-ynyl)-5,5-dimethyl-1-(*m*-toluidino)-1-imidazolin-4-one (**10b**): yield 38%; mp 109-111 °C; ^{1}H NMR δ= 1.38 (6 H, s, 5-Me), 1.97 (1 H, t, *J*= 2.6 Hz, ≡CH), 2.33 (3 H, s, Me), 2.68 (2 H, td, *J*= 6.9, 2.6 Hz, -C*H*$_2$-C≡CH), 3.83 (2 H, t, *J*= 6.9 Hz, >N-CH$_2$-), 4.75 (1 H, br s, NH), 6.75-7.22 (4 H, ov, aromatic-H). Anal. Found: C, 71.39; H, 7.08; N, 15.48%. Calcd for $C_{16}H_{19}N_3O$: C, 71.35; H, 7.11; N, 15.48%.

3-(But-3-ynyl)-5,5-dimethyl-2-tosylamino-1-imidazolin-4-one (**10d**): yield 71%; mp 149-151 °C; ^{1}H NMR δ= 1,44 (6 H, s, 5-Me), 1.76 (1 H, t, *J*= 2.6 Hz, ≡CH), 2.42 (3 H, s, Me), 2.50 (2 H, td, *J*= 6.9, 2.6 Hz, -C*H*$_2$-C≡CH), 3.70 (2 H, t, *J*= 6.9 Hz, >N-CH$_2$-), 7.29, 7.83, 8.07 (total 4 H, aromatic-H). Anal. Found: C, 57.68; H, 5.73; N, 12.52%. Calcd for $C_{16}H_{19}N_3O_3S$: C, 57.64; H, 5.74; N, 12.60%.

2-Anilino-3-(but-2-ynyl)-5,5-dimethyl-1-imidazolin-4-one (**11a**): yield 45%; mp 125-126 °C; ^{1}H NMR δ= 1.38 (6 H, s, 5-Me), 1.81 (3 H, t, *J*= 2.3 Hz, ≡C-Me), 4.37 (2 H, q, *J*= 2.3 Hz, >N-CH$_2$-), 4.79 (1 H, br s, NH), 6.98-7.34 (5 H, ov, Ph). Anal. Found: C, 70.75; H, 6.80; N, 16.30%. Calcd for $C_{15}H_{17}N_3O$: C, 70.56; H, 6.71; N, 16.46%.

3-(But-2-ynyl)-5,5-dimethyl-2-tosylamino-1-imidazolin-4-one (**11d**): yield 80%; mp 176-177 °C; ^{1}H NMR δ= 1.45 (6 H, s, 5-Me), 1.71 (3 H, t, *J*= 2.3 Hz, ≡CH), 2.43 (3 H, s, Me), 4.23 (2 H, q, *J*= 2.3 Hz, >N-CH$_2$), 7.30, 7.87 (total 4 H, aromatic-H), 8.05 (1 H, br s, NH). Anal. Found: C, 57.47; H, 5.73; N, 12.58%. Calcd for $C_{16}H_{19}N_3O_3S$: C, 57.64; H, 5.74; N, 12.60%.

2-Anilino-5,5-dimethyl-3-(3-phenylprop-2-ynyl)-1-imidazolin-4-one (**12a**): yield 22%; mp 70-72 °C; ^{1}H NMR δ= 1.42 (6 H, s, 5-Me), 4.67 (3 H, ov, >N-CH$_2$- and NH), 6.97-7.48 (10 H, ov, Ph). Anal. Found: C, 75.52; H, 6.38; N, 13.50%. Calcd for $C_{20}H_{19}N_3O$: C, 75.67; H, 6.03; N, 13.24%.

5,5-Dimethyl-3-(3-phenylprop-2-ynyl)-2-tosylamino-1-imidazolin-4-one (**12d**): yield 82%; mp 181-182 °C; ^{1}H NMR δ= 1.47 (6 H, s, 5-Me), 2.36 (3 H, s, Me), 4.51 (2 H, s, >N-CH$_2$-), 7.18, 7.25-7.31, 7.86 (total 9 H, aromatic-H), 8.07 (1 H, br s, NH). Anal. Found: C, 63.67; H, 5.32; N, 10.67%. Calcd for $C_{21}H_{21}N_3O_3S$: C, 63.78; H, 5.35; N, 10.63%.

Iodocyclization of 3-Alkynyl-1-imidazolin-4-ones 9-12. General Procedures: To a solution of imidazolinone **9a** (0.121 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. The residue was subjected to column chromatography on silica gel [hexane-ethyl acetate (1/1)] to afford 5-*exo* cyclization product **13a** (0.141 g, 77%).

2-[(*E*)-Iodomethylene]-6,6-dimethyl-1-phenyl-2,3-dihydro-1*H*-imidazo[1,2-*a*]imidazol-5(6*H*)-one (**13a**): colorless needles (hexane-benzene); mp 167-168 °C; IR cm^{-1}: 1730 (CO), 1630 (C=N); ^{1}H NMR δ= 1.41 (6 H, s, 5-Me), 4.34 (2 H, d, *J*= 2.3 Hz, 3-H), 5.28 (1 H, t, *J*= 2.3 Hz, =CHI), 7.38-7.54 (5 H, ov, Ph); ^{13}C NMR δ= 24.9 (6-Me), 46.1 (=CHI), 47.5 (3-C), 74.5 (6-C), 126.5, 128.5, 130.2, 133.2 (Ph-C), 145.8 (2-C), 156.8

(7a-C), 179.8 (5-C); MS *m/z:* 367 (M^+), 352 (M^+ - Me), 339 (M^+ - CO). Anal. Found: C, 45.74; H, 3.85; N, 11.44%. Calcd for $C_{14}H_{14}IN_3O$: C, 45.79; H, 3.84; N, 11.44%.

2-[*(E)*-Iodomethylene]-6,6-dimethyl-1-(1-naphthyl)-2,3-dihydro-1*H*-imidazo[1,2-*a*]imidazol-5(6*H*)-one (**13c**): colorless crystals; mp 169-170 °C (without recrystallization); IR cm^{-1}: 1730 (CO), 1640 (C=N); ^1H NMR δ= 1.39, 1.42 (each 3 H, each s, 5-Me), 4.54 (1 H, dd, *J*= 16.1, 2.2 Hz, 3-H), 4.60 (1 H, dd, *J*= 16.1, 2.6 Hz, 3-H), 4.76 (1 H, dd, *J*= 2.6, 2.2 Hz, =CHI), 7.52-7.99 (7 H, ov, aromatic-H); ^{13}C NMR δ= 24.8, 25.1 (6-Me), 46.4 (3-C), 47.3 (=CHI), 74.6 (6-C), 122.2, 125.9, 126.8, 127.0, 127.4, 128.7, 129.1, 129.3, 134.9 (naphthyl-C), 146.5 (2-C), 157.3 (7a-C), 179.9 (5-C); MS *m/z:* 417 (M^+), 402 (M^+ - Me), 290 (M^+ - I). Anal. Found: C, 51.90; H, 3.83; N, 9.99%. Calcd for $C_{18}H_{16}IN_3O$: C, 51.82; H, 3.87; N, 10.07%.

3-[*(E)*-2,3-Diiodoprop-2-enyl]-5,5-dimethyl-2-(1-naphthyl)amino-1-imidazolin-4-one (**14c**) was also obtained in a trace and its structure was supported by the following ^1H NMR spectral data: δ= 1.44 (6 H, s, 5-Me), 4.64 (2 H, d, *J*= 1.6 Hz, >N-CH_2-), 4.76 (1 H, br s, NH), 7.04-8.21, ov, =CHI and naphthyl-H).

2-[*(E)*-Iodomethylene]-6,6-dimethyl-1-tosyl-2,3-dihydro-1*H*-imidazo[1,2-*a*]imidazol-5(6*H*)-one (**13d**): colorless needles (ethanol); IR cm^{-1}: 1725 (CO), 1635 (C=N), 1370, 1175 (SO_2); ^1H NMR δ= 1.40 (6 H, s, 6-Me), 2.46 (3 H, s, Me), 4.11 (2 H, d, *J*= 2.4 Hz, 3-H), 6.88 (1 H, t, *J*= 2.4 Hz, =CHI), 7.36, 7.93 (total 2 H, aromatic-H); ^{13}C NMR δ= 21.7 (Me), 24.4 (6-Me), 47.4 (3-C), 60.2 (=CHI), 75.2 (6-C), 127.9, 130.0, 133.8, 146.5 (aromatic-C), 138.6 (2-C), 154.2 (7a-C), 179.4 (5-C); MS *m/z:* 445 (M^+), 417 (M^+ - CO), 381 (M^+ - SO_2), 318 (M^+ - I). Anal. Found: C, 40.52; H, 3.61; N, 9.43%. Calcd for $C_{15}H_{16}IN_3O_3S$: C, 40.46; H, 3.62; N, 9.44%.

3-[*(E)*-2,3-Diiodoprop-2-enyl]-5,5-dimethyl-1-imidazolin-4-one (**15d**): colorless plates (hexane-benzene); mp 156-157 °C; IR cm^{-1}: 3320 (NH), 1770 (CO), 1620 (C=N), 1380, 1120 (SO_2); ^1H NMR δ= 1.51 (6 H, s, 5-Me), 2.42 (3 H, s, Me), 4.36 (2 H, d, *J*= 1.5 Hz, >N-CH_2-), 7.10 (1 H, t, *J*= 1.5 Hz, =CHI), 7.28, 7.84 (total 4 H, aromatic-H), 8.02 (1 H, br s, NH); ^{13}C NMR δ= 21.5 (Me), 24.8 (5-Me), 49.4 (>N-CH_2-), 60.6 (5-C), 83.0 (=CHI), 95.7 (-*C*I=CHI), 126.4, 129.3, 139.1, 143.1 (aromatic-C), 153.6 (2-C), 175.1 (4-C); MS *m/z:* 573 (M^+), 446 (M^+ - I). Anal. Found: C, 31.41; H, 3.00; N, 7.21%. Calcd for $C_{15}H_{17}I_2N_3O_3S$: C, 31.43; H, 2.99; N, 7.33%.

7-[*(E)*-Iodomethylene]-2,2-dimethyl-8-phenyl-5,6,7,8-tetrahydroimidazo[1,2-*a*]pyrimidin-3(2*H*)-one (**16a**): colorless prisms (hexane-benzene); mp 165 °C (dec.); IR cm^{-1}: 1730 (CO); 1630 (C=N), ^1H NMR δ= 1.29 (6 H, s, 2-Me), 3.04 (2 H, t, *J*= 6.3 Hz, 6-H), 3.71 (2 H, t, 5-H), 4.86 (1 H, s, =CHI), 7.25-7.52 (5 H, ov, Ph); ^{13}C NMR δ= 24.6 (2-Me), 29.4 (6-C), 36.3 (5-C), 56.4 (=CHI), 67.0 (2-C), 128.7, 129.0, 130.1, 137.7 (Ph-C), 142.3 (7-C), 149.7 (8a-C), 183.8 (3-C). Anal. Found: C, 47.14; H, 4.21; N, 10.92%. Calcd for $C_{15}H_{16}IN_3O$: C, 47.26; H, 4.23; N, 11.02%.

7-[*(E)*-Iodomethylene]-2,2-dimethyl-8-(*m*-tolyl)-5,6,7,8-tetrahydroimidazo[1,2-*a*]pyrimidin-3(2*H*)-one (**16b**): colorless needles (hexane-benzene); mp 158-159 °C; IR cm^{-1}: 1720 (CO), 1630 (C=N); ^1H NMR δ= 1.29 (6 H, s, 2-Me), 2.38 (3 H, s, Me), 3.03 (2 H, t, *J*= 6.3 Hz, 6-H), 3.70 (2 H, t, *J*= 6.3 Hz, 5-H), 4.83 (1 H, s, =CHI), 7.04-7.40 (4 H, ov, aromatic-H); ^{13}C NMR δ= 21.4 (Me), 24.6 (2-Me), 29.4 (6-C), 36.2 (5-C), 56.1 (=CHI), 67.0 (2-C), 126.0, 129.5, 129.7, 129.9, 137.6 (aromatic-C), 142.3 (7-C), 149.7 (8a-C), 183.8 (3-C). Anal. Found: C, 48.90; H, 4.52; N, 10.49%. Calcd for $C_{16}H_{18}IN_3O$: 48.62; H, 4.59; N, 10.63%.

7-[*(E)*-Iodomethylene]-2,2-dimethyl-8-tosyl-5,6,7,8-tetrahydroimidazo[1,2-*a*]pyrimidin-3(2*H*)-one (**16d**): colorless prisms (ethanol); mp 147 °C (dec.); IR cm^{-1}: 1720 (CO), 1620 (C=N), 1360, 1170 (SO_2); ^1H NMR δ= 1.24 (6 H, s, 2-Me), 2.43 (3 H, s, Me), 2.66 (2 H, t, *J*= 6.6 Hz, 6-H), 3.44 (2 H, t, *J*= 6.6 Hz, 5-H), 6.85 (1 H, s, =CHI), 7.30, 7.88 (each 2H, each ov, aromatic-H); ^{13}C NMR δ= 21.6 (Me), 24.2 (2-Me), 28.2 (6-C), 38.2 (5-C), 67.3 (2-C), 80.7 (=CHI), 128.7, 129.4, 134.8, 145.5 (aromaric-C), 135.4 (7-C), 146.8 (8a-C),

183.4 (3-C). Anal. Found: C, 41.87; H, 4.02; N, 9.04%. Calcd for $C_{16}H_{18}IN_3O_3S$: C, 41.84; H, 3.95; N, 9.15%.

3-[*(E)*-3,4-Diiodidobut-3-enyl]-5,5-dimethyl-2-tosylamino-1-imidazolin-4-one (**17d**): colorless needles (hexane-benzene); 191-192 °C; IR cm^{-1}: 3380 (NH), 1760 (CO), 1635 (C=N), 1390. 1130 (SO_2); ^1H NMR δ= 1.46 (6 H, s, 5-Me), 2.42 (3 H, s, Me), 2.82 (2 H, t, *J*= 5.9 Hz, -CH_2-CI=), 3.77 (2 H, t, *J*= 5.9 Hz, >N-CH_2-), 6.63 (1 H, s, =CHI), 7.28, 7.88 (each 2 H, each ov, aromatic-H), 8.02 (1 H, br s, NH); ^{13}C NMR δ= 21.5 (Me), 24.7 (5-Me), 37.1 (-*C*H_2-CI=), 43.6 (>N-CH_2-), 60.1 (5-C), 81.9 (=CHI), 98.2 (-CH_2-*C*I=), 126.6, 129.3, 139.1, 143.2 (aromatic-C), 154.6 (2-C), 175.9 (4-C). Anal. Found: C, 32.91; H, 3.31; N, 7.12%. Calcd for $C_{16}H_{19}IN_3O_3S$: C, 32.73; H, 3.26; N, 7.16%.

2-[*(E)*-1-Iodoethylidene]-6,6-dimethyl-1-phenyl-2,3-dihydro-1*H*-imidazo[1,2-*a*]imidazol-5(6*H*)-one (**18a**): this compound could not be isolated in a pure form. However, its structure was assigned on the basis of its NMR specral data: ^1H NMR δ= 1.38 (6 H, s, 6-Me), 1.96 (3 H, t, *J*= 2.0 Hz, =CIMe), 4.42 (2 H, q, *J*= 2.0 Hz, 3-H), 7.33-7.64 (5 H, ov, Ph); ^{13}C NMR δ= 24.9 (6-Me), 27.9 (=CI*Me*), 50.6 (5-C), 70.5 (=*C*IMe), 74.2 (6-C), 126.8, 128.1, 129.7, 133.2 (Ph-C), 138.0 (2-C), 180.1 (5-C).

6-Iodo-2,2,7-trimethyl-8-phenyl-5,8-dihydroimidazo[1,2-*a*]pyrimidin-3(2*H*)-one (**19a**): colorless needles (hexane-benzene); mp 184 °C (dec.); IR cm^{-1}: 1720 (CO), 1620 (C=N); ^1H NMR δ= 1.28 (6 H, s, 2-Me), 1.86 (3 H, t, *J*= 2.0 Hz, 7-Me), 4.37 (2 H, q, *J*= 2.0 Hz, 5-H), 7.23-7.48 (5 H, ov, Ph); ^{13}C NMR δ= 24.3 (7-Me), 24.6 (2-Me), 49.3 (5-C), 60.5 (6-C), 66.7 (2-C), 128.8, 129.4, 129.6, 135.7 (Ph-C), 138.3 (7-C), 149.1 (8a-C), 183.7 (3-C). Anal. Found: C, 50.36; H, 4.48; N, 10.22%. Calcd for $C_{15}H_{16}INO_3 \cdot 1/3C_6H_6$: C, 52.12; H, 4.42; N, 10.31%.

6-Iodo-2,2,7-trimethyl-8-tosyl-5,8-dihydroimidazo[1,2-*a*]pyrimidin-3(2*H*)-one (**22d**): colorless needles (hexane-benzene); mp 147 °C (dec.); IR cm^{-1}: 1730 (CO), 1650 (C=N), 1360, 1180 (SO_2); ^1H NMR δ= 1.31 (6 H, s, 2-Me), 2.44 (3 H, t, *J*= 1.7 Hz, 7-Me), 2.46 (3 H, s, Me), 3.89 (2 H, q, *J*= 1.7 Hz, 5-H), 7.34, 7.86 (each 2 H, each ov, aromatic-H); ^{13}C NMR δ= 21.7 (Me), 23.7 (2-Me), 26.1 (7-Me), 48.7 (5-C), 70.2 (2-C), 81.7 (6-C), 128.1, 129.9, 135.2, 145.7 (aromatic-C), 137.1 (7-C), 147.7 (8a-C), 183.0 (3-C). Anal. Found: C, 41.63; H, 4.00; N, 8.88%. Calcd for $C_{16}H_{18}IN_3O_3S$: C, 41.84; H, 3.95; N, 9.15%.

3-[*(E)*-2,3-Diiodobut-2-enyl)]-5,5-dimethyl-2-tosylamino-1-imidazolin-4-one (**23d**): colorless plates (ethanol); mp 201 °C (dec.); IR cm^{-1}: 3340 (NH), 1760 (CO), 1635 (C=N), 1390, 1135 (SO_2); ^1H NMR δ= 1.50 (6 H, s, 5-Me), 2.42 (3 H, s, Me), 2.51 (3 H, t, *J*= 1.0 Hz, =CIMe), 4.47 (2 H, q, *J*= 1.0 Hz, >N-CH_2-), 7.28, 7.83 (each 2 H, each ov, aromatic-H), 8.05 (1 H, br s, NH); ^{13}C NMR δ= 21.5 (Me), 24.8 (5-Me), 40.3 (=CI*Me*), 54.4 (>N-CH_2-), 60.6 (5-C), 95.4, 97.2 (-*C*I=*C*IMe), 126.4, 129.3, 139.2, 143.0 (aromatic-C), 153.7 (2-C), 175.3 (4-C); MS *m/z:* 587 (M^+), 460 (M^+ - I), 380, 334. Anal. Found: C, 32.83; H, 3.26; N, 7.09%. Calcd for $C_{16}H_{19}IN_3O_3S$: C, 32.73; H, 3.26; N, 7.16%.

3-[*(E)*-2,3-Diiodo-3-phenylprop-2-enyl]-5,5-dimethyl-2-tosylamino-1-imidazolin-4-one (**24d**): colorless prisms (ethanol); mp 185-186 °C; IR cm^{-1}: 3320 (NH), 1760 (CO), 1630 (C=N), 1390, 1130 (SO_2); ^1H NMR δ= 1.53 (6 H, s, 5-Me), 2.42 (3 H, s, Me), 4.62 (2 H, s, >N-CH_2-), 6.91-6.93, 7.24-7.30, 7.89 (total 9 H, ov, aromatic-H), 8.08 (1 H, br s, NH); ^{13}C NMR δ= 22.0 (Me), 25.3 (5-Me), 54.5 (>N-CH_2-), 61.1 (=*C*I-Ph), 98.9 (-CI=), 127.0, 128.3, 128.8, 128.9, 129.8, 139.7, 143.6 (aromatic-C), 154.1 (2-C), 175.6 (4-C). Anal. Found: C,39.01; H, 3.33; N, 6.43%. Calcd for $C_{21}H_{21}I_2N_3O_3S$: C, 38.85; H, 3.26; N, 6.47%.

Iodocyclization of 3-Allenyl-1-imidazolin-4-ones 29d and 30d. Preparation of 3-Allenyl-1-imidazolin-4-one 29d: A solution of imidazolinone **12d** (0.160 g, 0.5 mmol) and *t*-BuOK (0.067 g, 0.6 mmol) in *t*-BuOH (6 ml) was heated at 30 °C for 2 h. The solvent was evaporated and the residue 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 (1/1)] to afford 3-allenyl imidazolinone **29d** (0.078 g, 50%).

The acetylene-allene isomerization of other imidazolinones under similar conditions was carried out to afford the desired products (monitored by TLC). However, usual work-up gave only the starting 3-alkynyl imidazolinones except for **30d**.

Iodocyclization of 3-Allenyl-1-imidazolin-4-ones 29d and 30d: To a solution of imidazolinone **29d** (0.120 g, 0.37 mmol) in DME (5 ml) was added iodine (0.286 g, 1.1 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. The residue was subjected to column chromatography on silica gel [hexane-ethyl acetate (1/1)] to afford 6-*endo* cyclization product **31d** (0.059 g, 36%).

5,5-Dimethyl-3-(propa-1,2-dienyl)-2-tosylamido-1-imidazolin-4-one (**29d**): colorless prisms (hexane-benzene); mp 175-176 °C; IR cm^{-1}: 3320 (NH), 1760 (CO), 1620 (C=N, C=C), 1380, 1130 (SO_2); ^1H NMR δ= 1.45 (6 H, s, 5-Me), 2.43 (3 H, s, Me), 5.38 (2 H, d, *J*= 6.9 Hz, =CH_2), 6.58 (1 H, t, *J*= 6.9 Hz, >N-CH=), 7.31, 7.86 (each 2 H, each ov, aromatic-H), 8.21 (1 H, br s, NH); ^{13}C NMR δ= 21.5 (Me), 24.6 (5-Me), 60.5 (5-C), 85.8 (=CH_2), 88.7 (>N-CH=), 126.3, 129.5, 139.0, 143.3 (aromatic-C), 152.5 (2-C), 173.5 (4-C), 204.0 (-CH=*C*=CH_2); MS *m/z:* 319 (M^+), 164 (M^+ - Ts). Anal. Found: C, 56.41; H, 5.40; N, 13.20%. Calcd for $C_{15}H_{17}N_3O_3S$: C, 56.41; H, 5.37; N, 13.16%.

5,5-Dimethyl-3-(3-phenylpropa-1,2-dienyl)-2-tosylamido-1-imidazolin-4-one (**30d**): pale yellow prisms (hexane-benzene); mp 133-135 °C; IR cm^{-1}: 3320 (NH), 1760 (CO), 1620 (C=N, C=C), 1275, 1135 (SO_2); ^1H NMR δ= 1.47 (6 H, s, 5-Me), 2.39 (3 H, s, Me), 6.69 (1 H, d, *J*= 6.3 Hz, =C*H*-Ph), 6.90 (1 H, d, *J*= 6.3 Hz, -CH=), 7.20, 7.24-7.37, 7.76 (total 9 H, aromatic-H), 8.15 (1 H, br s, NH); ^{13}C NMR δ= 21.5 (Me), 24.7, 24.8 (5-Me), 60.0 (5-C), 91.3 (>N-CH=), 104.1 (=*C*H-Ph), 126.3, 127.8, 128.0, 128.6, 129.3, 132.7, 138.9, 143.1 (aromatic-C), 152.4 (2-C), 173.4 (4-C), 200.3 (-CH=*C*=CH-Ph). Anal. Found: C, 63.94; H, 5.18; N, 10.66%. Calcd for $C_{21}H_{21}N_3O_3S$: C, 63.78; H, 5.35; N, 10.63%.

6-Iodo-2,2-dimethyl-8-tosyl-7,8-dihydroimidazo[1,2-*a*]pyrimidin-3(2*H*)-one (**31d**): colorless needles (hexane-benzene); mp 191-192 °C; IR cm^{-1}: 1730 (CO), 1660 (C=N), 1640 (C=C), 1360, 1170 (SO_2); ^1H NMR δ= 1.28 (6 H, s, 2-Me), 2.44 (3 H, s, Me), 4.53 (2 H, d, *J*= 1.7 Hz, 7-H), 6.96 (1 H, t, *J*= 1.7 Hz, 5-H), 7.33, 8.00 (each 2 H, each ov, aromatic-H); ^{13}C NMR δ= 21.7 (Me), 24.5 (2-Me), 53.0 (7-C), 67.5 (6-C), 68.0 (2-C), 124.2 (5-C), 128.9, 129.4, 134.2, 145.6 (aromatic-C), 143.1 (8a-C), 177.2 (3-C). Anal. Found: C, 40.95; H, 3.56; N, 9.33%. Calcd for $C_{15}H_{16}IN_3O_3S$: C, 40.46; H, 3.62; N, 9.44%.

6-Iodo-2,2-dimethyl-7-phenyl-8-tosyl-7,8-dihydroimidazo[1,2-*a*]pyrimidin-3(2*H*)-one (**32d**): colorless needles (hexane-benzene); mp 192-194 °C; IR cm^{-1}: 1740 (CO), 1640 (C=N), 1620 (C=C), 1350, 1170 (SO_2); ^1H NMR δ= 1.27, 1.33 (each 3 H, each s, 2-Me), 2.36 (3 H, s, Me), 6.04 (1 H, s, 7-H), 7.07-7.33 (8 H, ov, 5-H and aromatic-H), 7.69 (2 H, d, *J*= 8.3 Hz, aromatic-H); ^{13}C NMR δ= 21.5 (Me), 24.2, 24.5 (2-Me), 66.4 (7-C), 67.9 (2-C), 75.0 (6-C), 123.3 (5-C), 127.5, 128.7, 129.0 x 2, 134.8, 136.5, 144.7 (aromatic-C), 143.3 (8a-C), 177.4 (3-C). Anal. Found: C, 48.27; H, 3.85; N, 7.92%. Calcd for $C_{21}H_{20}IN_3O_3S$: C, 48.37; H, 3.84; N, 8.06%.

Computational Procedures: All iodonium ion intermediates **25-28** 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] on VAX 4000 in Ube Research Laboratory, Corporation Research & Development, Ube Industries Ltd. All iodonium ion intermediates were fully optimized unless otherwise indicated.

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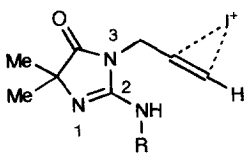
4 The fr(E) values of iodonium ions **25a** and **25d** are summarized.



Ion **25a** (R= Ph)			Ion **25d** (R= Ts)		
N(1)	:	0.015	N(1)	:	0.816
C(2)	:	0.044	C(2)	:	0.142
N(3)	:	0.000	N(3)	:	0.093
NHR	:	0.260	NHR	:	0.793
Ph (*ipso*)	:	0.491			
Ph (*ortho*)	:	0.158, 0.139			
Ph (*para*)	:	0.491			

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(*Received in Japan* 22 *January* 1996; *accepted* 22 *March* 1996)