YTTERBIUM TRIFLATE CATALYZED RING OPENING OF AZIRIDINES WITH AMINES†

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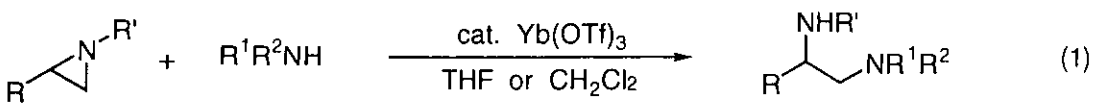
Abstract-Ring opening of aziridines with amines takes place readily in the presence of catalytic amounts of ytterbium triflate $Yb(OTf)_3$, giving the corresponding 1, 2-diamines regioselectively in good to high yields.

Vicinal diamines are synthetically, biologically, and medicinally important class of compounds.[1] One of the most straightforward synthetic procedures for the formation of 1,2-diamines is the ring opening of aziridines with amines.[2] However, this classical method has been disregarded primarily due to limitations of the reaction conditions: low nucleophilicity of amines requires elevated temperatures, and the unavailability of the aziridine starting materials. In recent years, several excellent methods for the synthesis of aziridines have been developed[3] and thus aziridines are now as readily available as epoxides. Accordingly, it was thought that the development of a new synthetic method for the formation of 1, 2-diamines *via* the ring opening of aziridines with amines would be timely and useful to significant number of synthetic chemists.[4]

We previously reported that ring opening of aziridines with amines takes place readily in the presence of catalytic amounts of ytterbium triflate $Yb(OTf)_3$, giving the corresponding 1, 2-diamines regioselectively in good to high yields (Eq 1).[5] Before our publication, a limited number of methodologies for catalytic ring opening of aziridines had been known; ring opening with cyanotrimethylsilane[6] or with acetone cyanohydrin[7] was catalyzed by lanthanoid derivatives. More recently, imidochromium complex catalyzed azidolysis of aziridines has been reported.[8] We now report the full details of the previous study.



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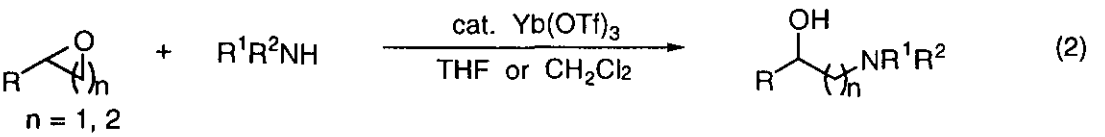
Results and Discussion

Crotti *et al.* and our group reported that ytterbium triflate catalyzed aminolysis reaction of epoxides,[9a, 10] oxetanes,[9b, 10] and ß-lactone,[10] giving the corresponding 1,2-, 1,3-amino alcohols, respectively, in good to high yields (Eq 2). We recognized in this study how efficiently the new catalyst[11] promotes the ring opening reaction. Based upon this observation, we investigated the



ring opening of aziridines with $Yb(OTf)_3$ catalyst. We initially chose *N*-tosylcyclohexeneimine (**1**) and benzylamine as a standard system. The results are shown in Table 1. The reaction of (**1**) with benzylamine in the absence of the catalyst was very sluggish; the ring opening product (**2**) was obtained in 20 % yield after 1 week at room temperature. Since aziridines have lower reactivity toward various nucleophiles than epoxides, larger amounts of the catalyst were used compared to that for epoxides.[9, 10] In every case, the corresponding diamine (**2**) was obtained in an essentially quantitative yield. As expected, the stereochemistry of the 1, 2-diamine (**2**) was trans. Not only THF (conditions A, B) but also CH_2Cl_2 (conditions C, D), which sometimes induced decomposition of the starting materials in the case of aminolysis of epoxides, can be used as a solvent. The ring opening reaction proceeded at room temperature (Entries 1 and 3), but the reaction was accelerated by refluxing. Other lanthanoid triflates, such as $La(OTf)_3$, $Sm(OTf)_3$, $Pr(OTf)_3$, and $Y(OTf)_3$, were also very effective to the ring opening reaction.[12]

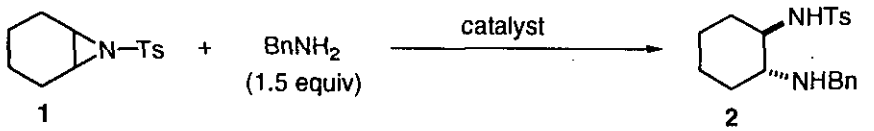


Table 1. Ring opening of 1 under various conditions.

Entry	Catalyst	Condition[a]	Reaction time, h	Yield[b], %
1	20 mol% $Yb(OTf)_3$	A	72	~100
2	20 mol% $Yb(OTf)_3$	B	24	~100
3	20 mol% $Yb(OTf)_3$	C	72	98
4	20 mol% $Yb(OTf)_3$	D	24	~100
5	20 mol% $La(OTf)_3$	A	72	~100
6	20 mol% $Sm(OTf)_3$	A	72	~100
7	20 mol% $Pr(OTf)_3$	A	72	~100
8	20 mol%$Y(OTf)_3$	A	72	~100

[a] Condition A : THF / room temperature. Condition B : THF / reflux. Condition C : CH_2Cl_2 / room temperature. Condition D : CH_2Cl_2 / reflux. [b] Isolated yield.

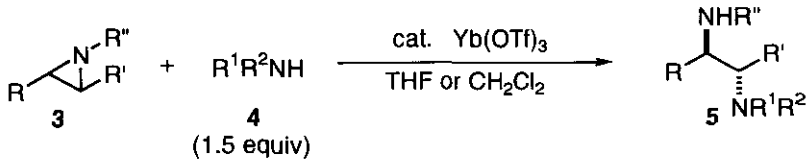
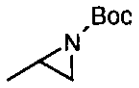
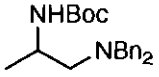
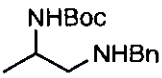
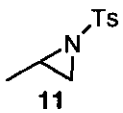
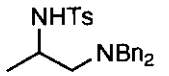
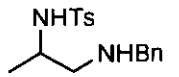
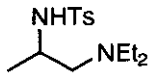
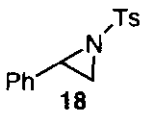
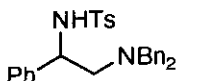
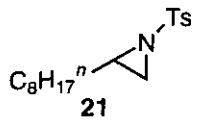
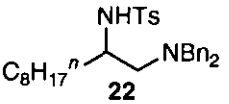
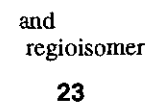
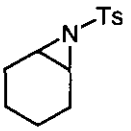
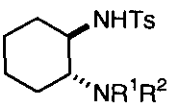
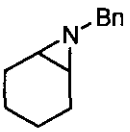
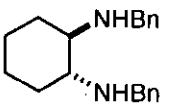
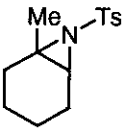
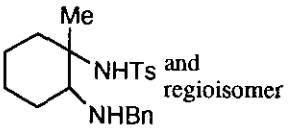


Table 2. $Yb(OTf)_3$ catalyzed ring opening of aziridines with amines.

Entry	Aziridine[a]	Amine(R^1R^2NH)	Catalyst	Condition[b]	Reaction time, h	Product and yield[c], %
1	 **6**	Bn_2NH	None	B	24	No reaction
						 **7** and regioisomer **8**
2	**6**	Bn_2NH	10 mol% $Yb(OTf)_3$	B	12	75 : 25 ~100
3	**6**	Bn_2NH	10 mol% $Yb(OTf)_3$	C	10	62 : 38 91
						 **9** and regioisomer **10**
4	**6**	$BnNH_2$	10 mol% $Yb(OTf)_3$	C	10	65 : 35 82
	 **11**					 **12** and regioisomer **13**
5		Bn_2NH	10 mol% $Yb(OTf)_3$	C	2	77 : 23 84
						 **14** and regioisomer **15**
6	**11**	$BnNH_2$	10 mol% $Yb(OTf)_3$	C	10	>99 : 1 75
						 **16** and regioisomer **17**
7	**11**	Et_2NH	10 mol% $Yb(OTf)_3$	C	8	>99 : 1 95
	 **18**					 **19** and regioisomer **20**
8		Bn_2NH	10 mol% $Yb(OTf)_3$	A	40	67 : 33 77[d]

(Continued.)

	 **21**				 **22**	 **23**	
9		Bn_2NH	10 mol% $Yb(OTf)_3$	A	72	>99 : 1	77^d
							
10	**1**	$BnNH_2$	20 mol% $Yb(OTf)_3$	D	24	**2**	~100
11	**1**	Et_2NH	20 mol% $Yb(OTf)_3$	D	24	**24**	82
12	**1**	$PhNH_2$	20 mol% $Yb(OTf)_3$	D	24	**25**	98
13	**1**		20 mol% $Yb(OTf)_3$	D	24	**26**	~100
14	**1**	Bn_2NH	20 mol% $Yb(OTf)_3$	D	48	No reaction	
							
15	**27**	$BnNH_2$	20 mol% $Yb(OTf)_3$	D	48	**28**	84
					 **30**	**31**	
16	**29**	$BnNH_2$	20 mol% $Yb(OTf)_3$	B	48	68 : 32	42^d
17	**29**	$BnNH_2$	20 mol% $Yb(OTf)_3$	D	48	63 : 47	49^d

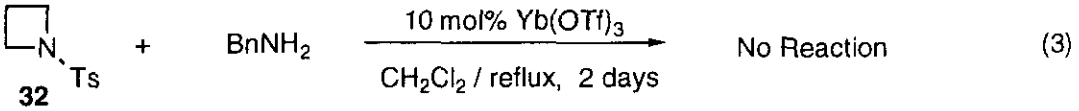
[a] Bn = $PhCH_2$, Boc = *t*-BuOCO, Ts = *p*-$MeC_6H_4SO_2$. [b] Condition A : THF / room temperature. Condition B : THF / reflux. Condition C : CH_2Cl_2 / room temperature. Condition D : CH_2Cl_2 / reflux. [c] Isolated yield. [d] Unidetified polymers were obtained as by-products.

Reaction of Various Aziridines

Since ytterbium triflate was found to be an effective catalyst for aminolysis of aziridines, next we examined the reaction of various aziridines (**3**) with amines (**4**) in the presence of this catalyst. The results are illustrated in Table 2. Since *N*-unprotected aziridines undergo ready oligomerization or polymerization, protection of the N-H group of the aziridines is essential for the ring opening reaction. As *N*-protecting groups, Boc (*t*-butyloxycarbonyl), benzyl and tosyl group were effective. Among them, the use of electron-withdrawing tosyl group resulted in rapid ring opening. Thus, we utilized this protecting group mainly in this research. It should be noted that an undesired side reaction[13] between the protecting groups and amines did not take place under the reaction conditions. $Yb(OTf)_3$ catalyzed ring opening was quite effective for mono- and di-substituted aziridines (Entries 1-15), but the reaction of tri-substituted aziridine (**29**) was sluggish and resulted in lower yield, being accompanied with unidentified polymers (Entries 16 and 17). As is apparent from the reaction of *N*-tosylcyclohexeneimine (**1**), various amines could be used as nucleophiles (Entries 10-13). However, dibenzylamine, relatively bulky and poorly nucleophilic amine, gave none of the desired product under the reaction conditions (Entry 14). Either cat.$Yb(OTf)_3$-THF (conditions A and B) or cat.$Yb(OTf)_3$-CH_2Cl_2 (conditions C and D) was effective for the ring opening of aziridines with amines. Either procedure gave the corresponding 1,2-diamines (**5**) regioselectively in good to high yields. The ring opening reaction proceeded even at ambient temperature (conditions A and C), although the reaction time was longer than that of procedures B and D. As expected, the amines attacked less hindered site of the aziridines. In general, the regioselectivity of the ring opening depends upon the structures of both substrates and amines. In Entries 6, 7 and 9, very high regioselectivity was accomplished, but a mixture of regioisomers was obtained in other cases (Entries 1-5, 8, 16 and 17).

Reaction with 1-Tosylazetidine

Now it is clear that $Yb(OTf)_3$ catalyzed ring opening of aziridines with amines proceeded smoothly to give the corresponding 1,2-diamines in good yields. Next we attempted the ring opening reaction of 1-tosylazetidine (**32**) with benzylamine in the presence of $Yb(OTf)_3$ catalyst. However, the reaction did not proceed at all: 1-tosylazetidine was recovered. (Eq 3) The $Yb(OTf)_3$ catalyzed ring opening of oxetanes with amines proceeded very smoothly.[9b, 10] A nitrogen analogue (**32**) of oxetane was proved to have lower reactivity toward an amine nucleophile.



CONCLUSION

We have found that $Yb(OTf)_3$ efficiently catalyzes ring opening of aziridines with amines regioselectively in good yields. Either THF or CH_2Cl_2 can be used as a solvent for the present

reaction. The reaction proceeds even at room temperature, although it takes longer reaction time in comparison with the reaction at reflux. The major regioisomers are derived via the attack of the amines to the less hindered site of aziridines.

EXPERIMENTAL

^{1}H Nmr spectra were recorded on a JEOL GSX-270 spectrometer. The chemical shifts are expressed in ppm downfield from the tetramethylsilane internal standard. All J values are in Hz. Ir spectra were recorded on a Hitachi Model 215. Mps were determined on a Yamato MP-21 capillary melting point apparatus. Mps were uncorrected.

Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under argon. Dichloromethane was distilled from calcium hydride under argon. The solvents were distilled before use. Most of the amines were distilled and stored under argon atmosphere. The lanthanoid triflate was prepared by literature procedure[14] and dried *in vacuo* before use. The starting aziridines were prepared by modified Blum's procedure[3b] (The refluxing benzene was used instead of ether.) and Evans' method.[3c] All reactions were conducted under argon atmosphere.

Typical procedure for the condition A

To a solution of $Yb(OTf)_3$ (62 mg, 0.10 mmol) in THF (1.0 ml), dibenzylamine (0.29 ml, 1.5 mmol) was added. After being stirred for five min, *N*-tosyl-1,2-iminodecane (**21**) (309 mg, 1.0 mmol) was added. The reaction mixture was stirred at room temperature and monitored by tlc. After consumption of the starting material, distilled water was added. The organic layer was extracted with three portions of CH_2Cl_2, and the extract was washed with brine and dried over anhydrous Na_2SO_4. Subsequent filtration and removal of the solvents under reduced pressures gave the crude product, which was purified by silica gel column chromatography using *n*-hexane-AcOEt (15 : 1) as an eluent. *N,N*-Dibenzyl-[2-(4-methylbenzenesulfonyl)aminodecyl]amine (**22**) (496 mg) was obtained in 98% yield.

Typical procedure for the condition D

The reaction of *N*-tosylcyclohexeneimine with aniline is representative. To a solution of $Yb(OTf)_3$ (124 mg, 0.20 mg) in CH_2Cl_2 (2.0 ml), aniline (0.40 ml, 1.5 mmol) was added. The reaction mixture was stirred for five min. *N*-Tosylcyclohexeneimine (**1**) (251 mg, 1.0 mmol) was added. The mixture was refluxed. The reaction was monitored by tlc. After disappearance of the substrate, distilled water was added. The organic layer was extracted with three portions of CH_2Cl_2, and the extract was washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressures and the residue was purified by silica gel column chromatography using *n*-hexane-AcOEt (3 : 1) as an eluent to give *trans*-*N*-(4-methylbenzenesulfonyl) -2-anilinocyclohexamine (**25**) (338 mg) in 98% yield.

***trans*-*N*-Benzyl-*N'*-(4-methylbenzenesulfonyl)-1,2-cyclohexanediamine (2)**

white needle mp 86.5-87.3 °C : ^{1}H Nmr (270 MHz, $CDCl_3$), δ 7.72(2H, m), 7.17-7.36(7H, m), 3.75(1H, d, *J* = 12.8 Hz, PhC*H*$_2$), 3.56(1H, d, J = 12.8 Hz, PhC*H*$_2$), 2.67(1H, ddd, *J* = 4.0, 10.0,

10.0 Hz, NC*H*), 2.38(3H, s), 2.24(1H, ddd, *J* = 4.0, 10.0, 10.0 Hz, NC*H*), 2.13(2H, m), 1.67(2H, m), 1.38(1H, br s), 1.17(3H, m), 0.97(1H, m), ir (neat) 3260, 1600, 1500, 1330, 1160 cm^{-1}. Anal. Calcd for $C_{20}H_{26}N_2O_2S$: C, 67.00; H, 7.31; N, 7.81. Found : C, 67.12; H, 7.45; N, 7.90.

***N*,*N*-Dibenzyl-[2-(*t*-butyloxycarbonyl)aminopropyl]amine (7)**

colorless syrup : ^1H Nmr (270 MHz, $CDCl_3$), δ 7.19-7.37 (10H, m), 4.42 (1H, br s, N*H*), 3.82 (1H, brs, C*H*N), 3.64 (2H, d, *J* = 13.1 Hz, PhCH_2), 3.48 (2H, d, *J* = 13.2 Hz, PhCH_2), 2.38 (1H, dd, *J* = 8.0, 13.0 Hz, NCH_2), 2.30 (1H, dd, *J* = 6.2, 13.0 Hz, NCH_2) , 1.47 (9H, s, Bu^t), 1.05 (3H, d, *J* = 6.5 Hz, CH_3), ir(neat) 3350, 1710, 1700, 1460, 1370, 1180 cm^{-1}. Anal. Calcd for $C_{22}H_{30}N_2O_2$: C, 73.65; H, 8.83; N, 8.18. Found : C, 74.00; H, 8.86; N, 7.90.

***N*-*t*-Butyloxycarbonyl-[2-(*N*′,*N*′-dibenzylamino)propyl]amine (8)**

white solid, mp 72.5-73.1°C : ^1H Nmr (270 MHz, $CDCl_3$), δ 7.18-7.35 (10H, m), 4.92 (1H, br s, N*H*), 3.76 (2H, d, *J* = 13.5 Hz, PhCH_2), 3.35 (2H, d, *J* = 13.5 Hz, PhCH_2), 2.97-3.19 (2H, m, NCH_2), 2.82 (1H, m, NC*H*) , 1.43 (9H, s, Bu^t), 1.20 (3H, d, *J* = 6.5 Hz, CH_3), ir(neat) 3320, 1705, 1680, 1540, 1160, 750 cm^{-1}. Anal. Calcd for $C_{22}H_{30}N_2O_2$: C, 73.65; H, 8.83; N, 8.18. Found : C, 74.05; H, 8.80; N, 7.82

***N*-Benzyl-[2-(*t*-butyloxycarbonyl)aminopropyl]amine (9) and *N*-*t*-Butyloxycarbonyl-[2-(*N*′-benzylamino)propyl]amine (10)** (inseparable mixtures)

(9)

colorless syrup : ^1H Nmr (270 MHz, $CDCl_3$), δ 7.20-7.35 (5H, m), 4.67 (1H, br s, N*H*), 3.82 (1H, d, *J* = 13.0 Hz, PhCH_2), 3.78 (1H, m), 3.76 (1H, d, *J* = 13.0 Hz, PhCH_2), 2.66 (1H, dd, *J* = 5.0, 12.0 Hz, NCH_2), 2.60 (1H, dd, *J* = 6.5, 12.0 Hz, NCH_2) , 1.44 (9H, s, Bu^t), 1.14 (3H, d, *J* = 6.5 Hz, CH_3).

(10)

colorless syrup : ^1H Nmr (270 MHz, $CDCl_3$), δ 7.20-7.35 (5H, m), 4.95 (1H, br s, N*H*), 3.83(1H, d, *J* = 13.5 Hz, PhCH_2), 3.75 (1H, d, *J* = 13.5 Hz, PhCH_2), 3.20 (1H, m), 3.02 (1H, dd, *J* = 6.0, 13.5 Hz) , 2.85 (1H, ddq, *J* = 5.0, 6.0, 6.5 Hz, NC*H*), 1.44 (9H, s, Bu^t), 1.04 (3H, d, *J* = 6.5 Hz, CH_3), Ir(neat) as mixtures 3350, 1710, 1370, 1180 cm^{-1}.

Anal. Calcd for $C_{15}H_{24}N_2O_2$ as mixtuers : C, 68.15; H, 9.15; N, 10.60. Found : C, 68.86; H, 9.23; N, 10.47.

***N*,*N*-Dibenzyl-[2-(4-methylbenzenesulfonyl)amino]propylamine (12) and *N*-(4-Benzenesulfonyl)-[2-(*N*′,*N*′-dibenzylamino)propyl]amine (13)** (inseparable mixtures)

(12)

colorless syrup : ^1H Nmr (270 MHz, $CDCl_3$), δ 7.63 (2H, dt, *J* = 2.0, 8.5 Hz), 7.12-7.37 (12H, m), 5.09 (1H, br s, N*H*), 3.56(2H, d, *J* = 13.5 Hz, PhCH_2), 3.27 (1H, m), 3.19 (2H, d, *J* = 13.5 Hz, PhCH_2), 2.38 (1H, dd, *J* = 9.0, 13.0 Hz, NCH_2), 2.34 (3H, s), 2.25 (1H, dd, *J* = 5.0, 13.0 Hz, NCH_2) , 1.06 (3H, d, *J* = 6.1 Hz, CH_3).

(13)

corless syrup : ^1H Nmr (270 MHz, $CDCl_3$), δ 7.83 (2H, dt, *J* = 1.7, 8.0 Hz), 7.12-7.37 (12H, m), 3.56 (2H, d, *J* = 13.5 Hz, PhCH_2), 3.19 (1H, d, *J* = 13.5 Hz, PhCH_2), 2.83 (1H, m), 2.62 (1H, d, *J* = 7.0 Hz) , 2.45 (3H, s), 2.23 (1H, d, *J* = 4.7 Hz), 1.26 (3H, d, *J* = 5.5 Hz, CH_3).

Ir(neat) as mixtures 3480, 1600,1506, 1340, 1170, 1100 cm^{-1}. Anal. Calcd for $C_{24}H_{28}N_2O_2S$ as mixtuers : C, 70.55; H, 6.91; N, 6.86. Found : C, 70.53; H, 6.84; N, 6.72.

***N*-Benzyl-[2-(4-methylbenzenesulfonyl)aminopropyl]amine (14)**

colorless syrup : ^1H Nmr (270 MHz, $CDCl_3$), δ 7.73 (2H, dt, J = 2.0, 8.2 Hz), 7.16-7.36 (7H, m), 3.56 (2H, s, PhC*H*2), 3.24 (1H, ddq, J = 4.5, 6.2, 8.0 Hz, C*H*N), 2.56 (1H, dd, J = 4.5, 12.0 Hz, NCH_2), 2.45 (1H, dd, J = 8.0, 12.0 Hz, NCH_2), 2.39 (3H, s), 1.10 (3H, d, J = 6.2 Hz, CH_3) , 1.47 (9H, s, Bu^t), 1.05 (3H, d, J = 6.5 Hz, CH_3), ir(CCl_4) 3270, 1600, 1450, 1340, 1170, 1100 cm^{-1}. Anal. Calcd for $C_{17}H_{22}N_2O_2S$: C, 64.32; H, 6.98; N, 8.83. Found : C, 63.93; H, 6.90; N, 8.87.

***N,N*-Diethyl-[2-(4-methylbenzenesulfonyl)aminopropyl]amine (16)**

colorless syrup : ^1H Nmr (270 MHz, $CDCl_3$), δ 7.76 (2H, dt, J = 1.5, 8.2 Hz), 7.30 (2H, m), 3.00 (1H, ddq, J = 5.0, 6.0, 10.0 Hz, C*H*N), 2.43 (3H, s), 2.25 (1H, dd, J = 5.0, 13.0 Hz, NCH_2), 2.20 (1H, dd, J = 8.0, 13.0 Hz, NCH_2), 2.14-2.37 (4H, ddq*2, J = 7.0, 13.0 Hz, CH_3CH_2) , 1.16 (3H, d, J = 6.0 Hz), 0.86 (6H, t, J = 7.0 Hz, CH_3CH2), ir(CCl_4) 3270, 1600, 1330, 1160, 1100 cm^{-1}. Anal. Calcd for $C_{14}H_{24}N_2O_2S$: C, 54.12; H, 8.51; N, 9.85. Found : C, 58.68; H, 8.30; N, 9.56.

***N,N*-Dibenzyl-[2-(4-methylbenzenesulfonyl)amino]-2-phenylethylamine (19) and *N,N*-Dibenzyl-[2-(4-methylbenzenesulfonyl)amino]-1-phenylethylamine (20)** (inseparable mixtures)

(19)

colorless syrup : ^1H Nmr (270 MHz, $CDCl_3$), δ 6.88-7.52 (19H, m), 5.57 (1H, br s, TsN*H*), 4.31 (1H, dd, J = 4.5, 10.0 Hz, PhC*H*), 3.70 (2H, d, J = 13.0 Hz, $PhCH_2$), 3.27 (2H, d, J = 13.0 Hz, $PhCH_2$), 2.61 (1H, dd, J = 10.0, 13.0 Hz), 2.25 (1H, dd, J = 4.5, 13.0 Hz) , 2.29 (3H, s).

(20)

corless syrup : ^1H Nmr (270 MHz, $CDCl_3$), δ 6.88-7.52 (19H, m), 5.01 (1H, br s, TsN*H*), 3.73 (2H, d, J = 13.5 Hz, $PhCH_2$), 3.52-3.71 (2H, m), 3.01-3.12 (1H,m), 3.04 (2H, d, J = 13.5 Hz, $PhCH_2$), 2.73 (3H, s).

Ir(neat) as mixtures 3288, 1598, 1494, 1454, 1330, 1163 cm^{-1}. Anal. Calcd for $C_{29}H_{30}N_2O_2S$ as mixtuers : C, 74.00; H, 6.43; N, 5.95. Found : C, 74.37; H, 6.44; N, 5.85.

***N,N*-Dibenzyl-[2-(4-methylbenzenesulfonyl)aminodecyl]amine (22)**

colorless syrup : ^1H Nmr (270 MHz, $CDCl_3$), δ 7.68 (2H, dt, J = 1.5, 8.0 Hz), 7.15-7.36 (12H, m), 3.52 (2H, d, J = 13.0 Hz, $PhCH_2$), 3.30 (2H, d, J = 13.0 Hz, $PhCH_2$), 3.23 (1H, m), 2.40 (1H, dd, J = 12.5, 17.0 Hz, NCH_2), 2.36 (1H, dd, J = 13.0, 17.0 Hz, NCH_2) , 2.36 (3H, s), 1.43 (2H, q, J = 7.0 Hz), 1.14-1.34 (6H, m), 0.93-1.14 (6H, m), 0.88 (3H, t, J = 7.0 Hz), ir(neat) 3280, 1600, 1460, 1338, 1165, 1095, 820 cm^{-1}. Anal. Calcd for $C_{31}H_{42}N_2O_2S$: C, 73.47; H, 8.35; N, 5.53. Found : C, 73.52; H, 8.30; N, 5.53.

***trans*-*N*-(4-Methylbenzenesulfonyl)-2-(*N'*-diethylamino)cyclohexamine (24)**

colorless oil : ^1H Nmr (270 MHz, $CDCl_3$), δ 7.76 (2H, dt, J = 1.6, 8.0 Hz), 7.31 (2H, br d), 6.11 (1H, br s), 2.70 (1H, ddd, J = 4.0, 10.0, 10.0 Hz, NC*H*), 2.43 (3H, s) , 2.40 (1H, m), 2.33 (1H, m), 2.10-2.29 (4H, m), 1.74 (2H, m), 1.63 (2H, m), 0.91-1.31 (3H, m), 0.90 (6H, t, J = 7.0 Hz) , ir(neat) 3220, 1600, 1500, 1450, 1400, 1350, 1160, 1095 cm^{-1}. Anal. Calcd for $C_{17}H_{28}N_2O_2S$: C, 62.92; H, 8.69; N, 8.63. Found : C, 62.87; H, 8.72; N, 8.56.

***trans*-*N*-(4-Methylbenzenesulfonyl)-2-anilinocyclohexamine (25)**

colorless oil : ^{1}H Nmr (270 MHz, $CDCl_3$), δ 7.75 (2H, m), 7.31 (2H, m), 7.14 (2H, m), 6.71 (1H, m), 6.47 (2H, m), 4.84 (1H, br d, *J* = 5.1 Hz), 3.40 (1H, br s), 3.07 (1H, ddd, *J* = 3.8, 10.0, 10.0 Hz, NC*H*), 2.91 (1H, m) , 2.46 (3H, s), 2.03-2.20 (2H, m), 1.65 (2H, m), 1.55 (1H, m), 1.17-1.38 (2H, m), 0.94-1.11 (1H, m) , ir(neat) 3400, 3290, 1600, 1510, 1450, 1330, 1300, 1160, 900 cm^{-1}. Anal. Calcd for $C_{19}H_{24}N_2O_2S$: C, 66.25; H, 7.02; N, 8.13. Found : C, 66.12; H, 6.85; N, 8.06.

***trans*-*N*-(4-Methylbenzenesulfonyl)-2-(pyrrolidin-1-yl)cyclohexamine (26)**

colorless syrup : ^{1}H Nmr (270 MHz, $CDCl_3$), δ 7.75(2H, dt, *J* = 2.0, 8.0 Hz) , 7.30 (2H, dt, *J* = 1.0, 8.0 Hz), 2.60 (1H, ddd, *J* = 4.0, 10.0, 10.0 Hz, NC*H*), 2.43 (3H, s), 2.42 (1H, ddd, *J* = 3.0, 10.0, 10.0 Hz, NC*H*), 2.31 (2H, m), 2.08 (2H, m), 1.74 (2H, m), 1.45-1.71 (6H, m), 0.98-1.33 (4H, m) , ir(neat) 3260, 1600, 1500, 1410, 1360, 1330 1180 cm^{-1}. Anal. Calcd for $C_{17}H_{26}N_2O_2S$: C, 63.32; H, 8.13; N, 8.69. Found : C, 63.20; H, 8.05; N, 8.66.

***trans*-*N*,*N*′-Dibenzyl-1,2-cyclohexanediamine[15] (28)**

colorless oil : ^{1}H Nmr (270 MHz, $CDCl_3$), δ 7.18-7.33 (10H, m), 3.90 (2H, d, *J* = 13.0 Hz, PhCH_2), 3.66 (2H, d, *J* = 13.0 Hz, PhCH_2), 2.27 (2H, ddd, *J* = 2.1, 3.2, 8.0 Hz, NC*H*), 2.16 (2H, m) , 1.89 (2H, br s), 1.71 (2H, m), 1.23 (2H, m), 1.04 (2H, m), ir(neat) 3300, 1600, 1490, 1450, 1360, 1120, 1030 cm^{-1}. Anal. Calcd for $C_{20}H_{26}N_2$: C, 81.58; H, 8.90; N, 9.51. Found : C, 81.18; H, 8.68; N, 9.41.

***N*-(4-Methylbenzenesulfonyl)-2-(*N*′-benzyiamino)-1-methylcyclohexamine (30)**

yellowish solid : ^{1}H Nmr (270 MHz, $CDCl_3$), δ 7.60 (2H, dt, *J* = 1.7, 8.0 Hz), 7.16-7.42 (7H, m), 5.84 (1H, br s), 4.70 (1H, br s), 3.93 (1H, d, *J* = 13.0 Hz, PhCH_2), 3.62 (1H, d, *J* = 13.0 Hz, PhCH_2), 2.39 (3H, s), 2.29 (1H, dd, *J* = 4.0, 11.3 Hz, NC*H*), 1.95-2.13 (2H, m) , 1.68 (1H, m), 1.46 (1H, m), 1.18-1.31 (2H, m), 1.15 (3H, s), 0.78-1.18 (2H, m), ir(neat) 3320, 1450, 1380, 1330, 1160 cm^{-1}. Anal. Calcd for $C_{21}H_{28}N_2O_2S$: C, 67.71; H, 7.58; N, 7.52. Found : C, 67.42; H, 7.45; N, 7.80.

***N*-Benzylamino-2-[*N*′-(4-methylbenzenesulfonyl)]-1-methylcyclohexamine (31)**

yellowish solid : ^{1}H Nmr (270 MHz, $CDCl_3$), δ 7.70 (2H, dt, *J* = 1.5, 8.5 Hz), 7.09-7.36 (7H, m), 5.11 (1H, br s), 3.58 (1H, d, *J* = 12.2 Hz, PhCH_2), 3.36 (1H, d, *J* = 12.2 Hz, PhCH_2), 2.90 (1H, dd, *J* = 4.0, 10.5 Hz, NC*H*), 2.34 (3H, s) , 2.02 (1H, m), 1.52-1.74 (3H, m), 1.10-1.47 (4H, m), 1.07 (3H, s), ir(neat) 3350, 3250, 1600, 1490, 1440, 1320, 1160, 1070 cm^{-1}. Anal. Calcd for $C_{21}H_{28}N_2O_2S$: C, 67.71; H, 7.58; N, 7.52. Found : C, 67.60; H, 7.48; N, 7.51.

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REFERENCES AND NOTES

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