NOVEL REARRANGEMENT OF *cis*-*N*-ALKYL-3-PHENYLAZIRIDIN-2-YL PHENYL KETONE TOSYLHYDRAZONES WITH ETHYL ETHER-BORON TRIFLUORIDE. PREPARATION OF 1,2,5,6-TETRAHYDRO-1,2,3-TRIAZINE DERIVATIVES

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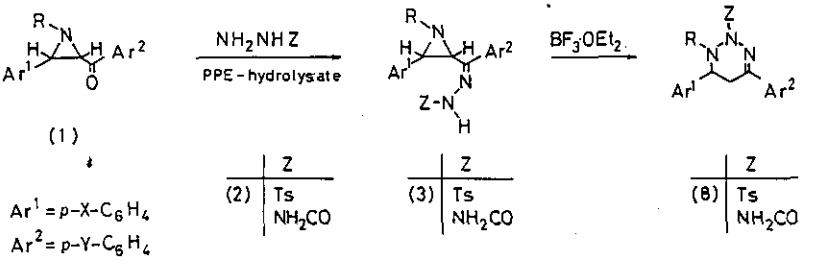
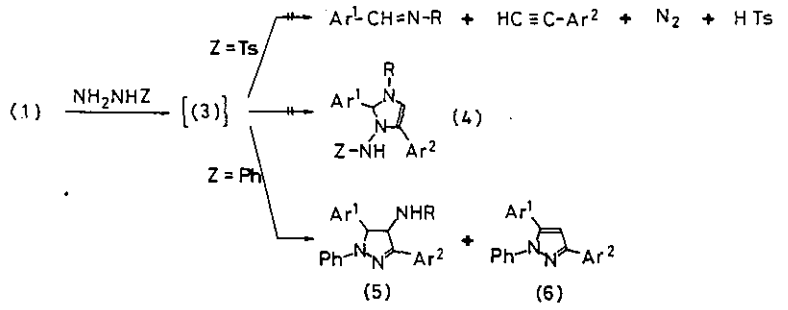
Abstract---1-Alkyl-4,6-diphenyl-1,2,5,6-tetrahydro-2-tosyl-1,2,3-triazine derivatives (8a-g,i-k) which had a new skeletal ring were obtained in moderate yield (77-49 %) by the rearrangement of *cis*-*N*-alkyl-3-phenylaziridin-2-yl phenyl ketone tosylhydrazones (3a-g,i-k) with ethyl ether-boron trifluoride(1/1) (7) in chloroform under room temperature. The starting materials (3a-l) were prepared in good yield (88-39%) by the condensation of *cis*-*N*-alkyl-3-phenylaziridin-2-yl phenyl ketones (1a-l) with tosylhydrazine (2) in chloroform in the presence of PPE (polyphosphoric acid ethyl ester) hydrolysate as a catalyst.

Relatively little is known about the preparation and the properties of tetrahydro-1,2,3-triazine derivatives. Arai *et al.*[1] reported the preparation of 4,6-disubstituted 1,4,5,6-tetrahydro-1,2,3-triazine 2-oxides. Previously Wladkowski *et al.*[2] treated the theoretical investigation of the proton-induced decomposition of 1,4,5,6-tetrahydro-1,2,3-triazine. Some studies on the thermal, photochemical rearrangement of various aziridinyl ketone hydrazone derivatives have been developed in this laboratory. We studied to see whether or not the Eschenmoser-type cleavage of *cis*-*N*-alkyl-3-phenylaziridin-2-yl phenyl ketone tosylhydrazone derivatives (3) produced arylalkynes. Consequently, it turned out that 3 were stable under neutral conditions at room temperature and didn't give those products even when the reaction mixtures of 3 were refluxed in dimethoxy-

ethane (Scheme 2). Recently we reported that a novel rearrangement of semicarbazones of *cis*-*N*-alkyl-3-phenylaziridin-2-yl phenyl ketones (1) in the presence of ethyl ether-boron trifluoride (1/1) (7) in dichloromethane gave 1-alkyl-2-carbamoyl-4,6-diphenyl-1,2,5,6-tetrahydro-1,2,3-triazine derivatives.[3] Cromwell *et al.*[4a,b] and Southwick *et al.*[4c] studied the condensation of 1 with phenylhydrazine in acetic acid and obtained the derivatives of 2-pyrazoline (5) and pyrazole (6) without isolating phenylhydrazone. We could isolate the semicarbazones of 1 in good yield, and so the products were allowed to react with 7 in place of acetic acid. In this paper we wish to describe that the rearrangement was applicable to the preparation of 1-alkyl-4,6-diphenyl-1,2,5,6-tetrahydro-2-tosyl-1,2,3-triazine derivatives (8a-g,i-k) and that 3a-l having a strained three-membered ring were prepared in moderate yield (Scheme 1).



Scheme 1



Scheme 2

RESULTS AND DISCUSSION

Preparation of tosylhydrazons (3) Ketones are readily converted to tosylhydrazones by use of tosyl hydrazine (2) in acidified ethanol, acetic acid and ocasionally neutral media for acid-sensitive carbonyl compounds.[5] The starting ketones (1) for the preparation of 3 were very unstable under acidic conditions. Nevertheless, the condensation of 1 with 2 was carried out under the weakly acidic conditions because the reaction rates of 1 with 2 in neutral media were low owing to carbonyl group unactivated by the conjugation between aziridinyl

ring and carbonyl group.[6] The condensation of 1 with 2 successfully was carried out by use of PPE[7] hydrolyzed partly (PPE-hydrolysate) and gave twelve hydrazones (3a-l). The catalyst was more useful than an unhydrolyzed PPE for an increase in yield. In EtOH / 0.01 % H_2SO_4 or CH_2Cl_2 / AcOH also the reaction was attempted, however the yields of 3 were very low. The preparation of 3 was run under room temperature in order to avoid the Cloke rearrangement (cyclopropylimine-pyroline rearrangement)[8] and the extended vinyl aziridine-pyroline rearrangement[9] (Scheme 2). The yields, the melting points, and the elemental analyses data of 3a-l were listed in Table 1. The spectral data of ^{1}H-nmr and ^{13}C-nmr were summarized in Table 2. The structural assignment of 3a-l was accomplished by comparing their spectra with those of semicarbazones which have already been reported.[3] That is to say, the ^{1}H-nmr spectra of 3 showed that 3 also had a aziridinyl ring, because the signals of 3 at *ca.* 3 ppm (AB pattern on the basis of methine protones at C2, C3 of 3) were similar to those of 1. The configuration at C2, C3 of 3 was assigned to *cis*-form on the ground of $J_{2,3}$ (5.6 -10.4 Hz).[10] The ^{1}H-nmr spectra of 3 exhibited a resonance peak shifted to low-field (near 12-13 ppm) of N-H hydrogen-bonded strongly with sulfonyl-oxygen atom of tosyl group. The ^{13}C-nmr spectra also supported the fact that 3 were the derivatives of aziridinyl ketone tosylhydrazone.

Table 1 Physical properties of compounds (3)

Compd.	R	X	Y	Yield/%	mp/℃	Found (Calcd)(%) C	H	N
(3a)	*i*-Pr	H	H	88	132-135	69.15	6.23	9.72
						(69.26	6.28	9.69)
(3b)	*c*-C_6H_{11}	H	H	73	117-119	70.87	6.55	8.89
						(71.01	6.60	8.87)
(3c)	$PhCH_2$	H	H	81	123-125	72.54	5.71	8.81
						(72.32	5.65	8.72)
(3d)	*t*-Bu	H	H	61	111-113	69.75	6.41	9.41
						(69.77	6.53	9.39)
(3e)	*c*-C_6H_{11}	H	CH_3O	69	123-125	68.90	6.50	8.13
						(69.16	6.60	8.34)
(3f)	*c*-C_6H_{11}	H	CH_3	63	121-124	71.54	6.77	8.66
						(71.43	6.82	8.62)
(3g)	*c*-C_6H_{11}	H	Cl	75	118-119	66.20	5.94	8.41
						(66.19	5.95	8.27)
(3h)	*c*-C_6H_{11}	H	NO_2	69	104-107	64.72	5.76	10.92

						(64.85	5.83	10.80)
(3i)	*c*-C_6H_{11}	CH_3O	H	39[a]	110-112	68.99	6.60	8.39
						(69.16	6.60	8.34)
(3j)	*c*-C_6H_{11}	CH_3	H	62	121-122	71.24	6.84	8.80
						(71.43	6.82	8.62)
(3k)	*c*-C_6H_{11}	Cl	H	87	129-132	66.15	6.01	8.31
						(66.19	5.95	8.27)
(3l)	*c*-C_6H_{11}	NO_2	H	76	123-125	64.94	5.86	11.06
						(64.85	5.83	10.80)

a The yield of 3i decreased because of the formation of by-products.

Table 2 Spectroscopic data of compounds (3)

	^{1}H-Nmr ($CDCl_3$): δ, J /Hz		^{13}C-Nmr ($CDCl_3$): δ		
	aziridinyl		aziridinyl		
Compd.	CH	NH	C2	C3	C=N
(3a)	2.89(1H,d,*J*=6.8)	12.42	46.5	48.1	143.4
	3.03(1H,d,*J*=6.8)				
(3b)	2.89(1H,d,*J*=7.0)	12.55	46.0	47.4	143.5
	3.00(1H,d,*J*=7.0)				
(3c)	3.02(1H,d,*J*=9.0)	12.11	46.3	48.6	143.4
	3.18(1H,d,*J*=9.0)				
(3d)	3.15(1H,d,*J*=10.4)	12.83	40.8	41.8	143.2
	3.33(1H,d,*J*=10.4)				
(3e)	2.87(1H,d,*J*=6.6)	12.30	45.9	47.4	143.2
	3.01(1H,d,*J*=6.6)				
(3f)	2.88(1H,d,*J*=6.8)	12.38	46.0	47.4	143.2
	3.02(1H,d,*J*=6.8)				
(3g)	2.88(1H,d,*J*=6.6)	12.35	45.9	47.4	142.4
	3.04(1H,d,*J*=6.6)				
(3h)	2.98(1H,d,*J*=6.6)	12.50	45.5	47.6	141.6
	3.13(1H,d,*J*=6.6)				
(3i)	2.88(1H,d,*J*=7.0)	12.60	45.7	46.9	143.1
	2.95(1H,d,*J*=7.0)				
(3j)	2.90(1H,d,*J*=7.6)	12.70	45.8	47.2	143.0
	3.00(1H,d,*J*=7.6)				
(3k)	3.02(2H,s)	12.34	45.7	46.5	143.0
(3l)	3.19(2H,s)	12.35	46.1	46.4	142.6

Preparation of 1,2,5,6-tetrahydro-1,2,3-triazines (8) The reaction of 3a-g,i-k with 1.4-fold molar of 7 in chloroform at room temperature gave 8a-g,i-k in

good yield. In the reaction of nitro-substituted 3h,l, 8h,l couldn't be isolated *owing to its decomposition during* the procedure of chromatography on silica gel. The yields, the melting points and the elemental analyses data of 8a-g,i-k were listed in Table 3. The spectral data of ir, ^{1}H-nmr and ^{13}C-nmr were summarized in Table 4 and Table 5. The structural assignment of tosyl derivatives (8a-g,i-k) was accomplished by comparing their spectra with those of carbamoyl derivatives reported in the preceeding paper.[3] Namely, the ^{1}H-nmr spectra of 8 showed *the signals at* δ= 3-4 *ppm* (AB *part of ABX pattern due to* methylene protones at C5) and at δ= 6-7 ppm (X part of ABX pattern due to methine protone at C6) and didn't have a signal due to a strongly hydrogen-bonded hydrogen in NH-S=O whose signal was present in spectra of 3. The ^{13}C-nmr spectrum of 8 at δ= 59.0-74.2 ppm was assigned to C6 methine carbon derived from the C3 carbon of 3. The chemical shifts were shifted to lower-field than those of the C3 carbon of 3. The *findings corresponded to the data in the literature;*[11] ^{13}*C-nmr chemical shift at* C2 carbon of *N*-methtylpiperizine is at δ = 57.2 ppm and those of *N*-methylaziridine is at δ = 28.5 ppm. In contrast with the mass spectra of semicarbazones, those of 8 were incapable of showing the existence of six-membered ring skeletone. However, 8 were assigned to 1,2,5,6-tetrahydro-1,2,3-triazine, because ^{1}H- and ^{13}C-nmr spectral pattern of 8 were similar to those of carbamoyl derivatives. The reaction rates (*ca.* 1-3 h) *of rearrangementof* 3 *with* 7 *were much* higher than those (*ca.* 1 d) of the corresponding semicarbazones. The findings indicated that their rates were accelerated by the electron-withdrawing Z. The yields of 8a-d decreased in the following order; *i*-Pr (65%)~ *c*-C_6H_{11} (68 %) > $PhCH_2$ (55 %)> *t*-Bu (49 %). The substituents effect of X,Y on the yields of 8 was lower than those of Z.

Table 3 Physical properties of compounds (8)

Compd.	R	X	Y	Yield/%	mp/℃	Found (Calcd)(%) C	H	N
(8a)	*i*-Pr	H	H	65	135-137	69.25	6.29	9.88
						(69.26	6.28	9.69)
(8b)	*c*-C_6H_{11}	H	H	68	137-139	71.18	6.55	8.90
						(71.01	6.60	8.87)
(8c)	$PhCH_2$	H	H	55	74- 77	72.38	5.69	8.72
						(72.32	5.65	8.72)
(8d)	*t*-Bu	H	H	49	181-185	69.59	6.58	9.34

						(69.77	6.53	9.39)
(8e)	c-C_6H_{11}	H	CH_3O	77	125-128	69.22	6.74	8.38
						(69.16	6.60	8.34)
(8f)	c-C_6H_{11}	H	CH_3	74	136-138	71.30	6.96	8.56
						(71.43	6.82	8.62)
(8g)	c-C_6H_{11}	H	Cl	68	171-173	66.00	6.06	8.09
						(66.19	5.95	8.27)
(8i)	c-C_6H_{11}	CH_3O	H	67	64- 67	69.03	6.65	8.40
						(69.16	6.60	8.34)
(8j)	c-C_6H_{11}	CH_3	H	71	171-173	71.08	6.78	8.64
						(71.43	6.82	8.62)
(8k)	c-C_6H_{11}	Cl	H	64	156-159	66.42	6.12	8.11
						(66.19	5.95	8.27)

Table 4 Spectroscopic data of compounds (8)

Compd.	Ir (KBr) ν /cm^{-1} (νSO_2)	^{1}H-Nmr ($CDCl_3$) δ, J /Hz 1,2,3-triazine CH_2[a]	CH[a]	other signals
(8a)	1360 1175	3.21 3.71	6.33	1.04(3H, d, J=6.0, CH_3), 1.24(3H, d, J=6.0, CH_3), 2.42(3H, s, tolyl CH_3), 2.4-3.0(1H, septet, J=6.0, i-propyl CH), 7.1-8.0(14H, m, Ph)
(8b)	1355 1175	3.20 3.75	6.34	0.8-2.6(11H, m, c-hexyl), 2.43(3H, s, tolyl CH_3), 7.0-8.1(14H, m, Ph)
(8c)	1355 1175	3.44 3.68	6.04	2.43(3H, s, tolyl CH_3), 3.35(2H, s, CH_2Ph), 7.0-8.1(19H, m, Ph)
(8d)	1350 1175	3.19 3.76	6.55	1.20(9H, s, t-butyl CH_3), 2.40(3H, s, tolyl CH_3), 7.0-8.0(14H, m, Ph)
(8e)	1355 1175	3.12 3.69	6.27	0.7-2.8(11H, m, c-hexyl), 2.40(3H, s, tolyl CH_3), 3.78(3H, s, OCH_3), 6.6-8.0(13H, m, Ph)
(8f)	1355 1180	3.13 3.69	6.24	0.6-2.6(11H, m, c-hexyl), 2.31(3H, s, tolyl CH_3), 2.38(3H, s, tolyl CH_3), 6.8-8.1(13H, m, Ph)
(8g)	1355 1175	3.15 3.66	6.30	0.7-2.5(11H, m, c-hexyl), 2.42(3H, s, tolyl CH_3), 7.0-8.1(13H, m, Ph)
(8i)	1360 1180	3.21 3.73	6.26	0.7-2.4(11H, m, c-hexyl), 2.42(3H, s, tolyl CH_3), 3.78(3H, s, OCH_3), 6.7-8.1(13H, m, Ph)
(8j)	1355 1175	3.18 3.70	6.22	0.6-2.5(11H, m, c-hexyl), 2.26(3H, s, tolyl CH_3), 2.37(3H, s, tolyl CH_3), 6.80-8.0(13H, m, Ph)
(8k)	1360 1175	3.13 3.72	6.25	0.6-2.6(11H, m, c-hexyl), 2.43(3H, s, tolyl CH_3), 7.0-8.1(13H, m, Ph)

a The coupling constants of ABX pattern were not calculated on account of their low peak resolution.

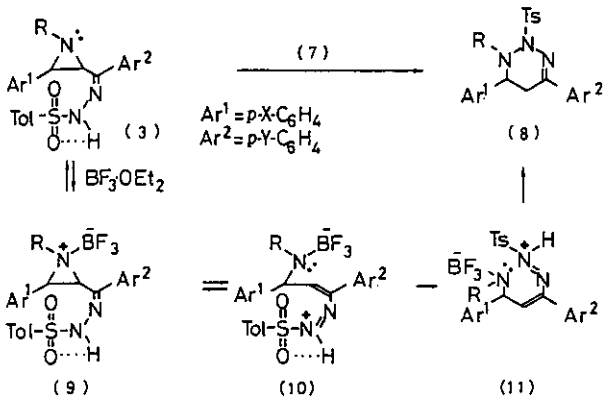
Table 5 ^{13}C −Nmr spectroscopic data of compounds(8)

^{13}C-Nmr ($CDCl_3$), δ

Compd.	CH_3	CH_2	1,2,3-triazine C(5)	C(6)	N-CH	aromatic CH			C(4°)		C=N
(8a)	20.9		39.2	51.5	72.7	124.8	126.8	127.9	135.6	135.9	146.2
	21.5					128.2	128.4	129.2	139.3	143.6	
	21.6					129.3					
(8b)	21.5	24.7 25.0	38.4	58.9	72.7	124.7	126.8	127.8	135.4	135.7	146.2
		25.7	30.6				128.1	128.4	129.2	139.5	143.6
		31.4									
(8c)	21.5	58.2	41.9	74.2		124.7	126.8	127.7	135.5	137.1	145.1
						128.1	128.2	128.3	138.4	143.8	
						128.5	128.8	129.3			
(8d)	21.6	55.6(4°)	37.5	69.7		124.9	126.7	127.7	135.4	136.2	148.4
	28.0					128.2	128.3	128.5	139.7	143.6	
						129.3	129.4				
(8e)	21.6	24.9 25.1	38.4	59.0	72.7	113.9	126.3	127.0	135.9	139.7	146.2
	55.4	25.8 30.8				127.9	128.2	128.5	143.6	160.7	
		31.5				129.3					
(8f)	21.3	24.9 25.1	38.4	59.1	72.8	124.8	127.0	128.0	132.8	135.9	146.5
	21.6	25.8 30.8				128.2	128.5	129.2	139.5	139.7	
		31.6				129.3			143.7		
(8g)	21.6	24.8 25.1	38.4	59.1	72.9	126.1	126.9	128.1	133.9	135.3	145.3
		25.8 30.8				128.2	128.6	128.8	135.7	139.5	
		31.5				129.4			143.9		
(8i)	21.5	24.9 25.1	38.4	59.0	72.5	113.9	124.8	128.1	131.7	135.5	146.3
	55.3	25.8 30.8				128.5	129.3		135.9	143.7	
		31.5							159.4		
(8j)	21.1	24.9 25.1	38.5	59.1	72.8	124.8	126.9	128.2	135.6	135.9	146.3
	21.6	25.9 30.8				128.5	129.2	129.3	136.7	137.7	
		31.6							143.7		
(8k)	21.6	24.9 25.1	38.5	59.2	72.2	124.8	128.2	128.5	133.9	135.3	146.6
		25.8 30.7				128.6	128.7	129.5	135.7	138.3	
		31.5							144.0		

Mechanism The tentative reaction paths to 8 were considered on the basis of the results obtained by Wladkowski *et al.*[2]. It was speculated that the rearrangement of 3 began with the coordination of boron trifluoride to aziridine ring nitrogen and that the formed aziridinum ring (9) was easy to open at the bond between C2 carbon and ring nitrogen.[12] Probably the attack of N-R nitrogen to Ts-N=N (10) in 11 may be a rate determining step. Therefore, we considered

that the yields of 8 decreased in case of either the electron-donating effect of R was low or the steric hindrance of them was high[13] (Scheme 3).



Scheme 3

EXPERIMENTAL

General. Nmr spectra were obtained on a JEOL JNM-EX90 and JNM-EX400 spectrometer. Ir spectra were recorded on a JASCO FT IR-3 spectrometer. CHN analyses were carried out at Elemental Analysis Laboratory, Institute for Chemical Reaction Science, Tohoku University.

Preparation of PPE (poly phosphoric acid ethyl ester) hydrolysate. To a chloroform solution of PPE prepared according to the method given in the literature[7] was added an equal volume of ice water, and the mixture was stirred overnight. The chloroform layer was separated. The aqueous layer was extracted ten times with chloroform. The combined chloroform extract was dried over anhydrous sodium sulfate, and evaporated *in vacuo*. The oily residue was used without further purification.

Preparation of *cis*-*N*-alkyl-3-(4-substituted phenyl)aziridin-2-yl phenyl ketone and *cis*-*N*-alkyl-3-phenylaziridin-2-yl 4-substituted phenyl ketones (1). All of the starting materials were prepared according to the literature.[14]

Preparation of *cis*-*N*-alkyl-3-(4-substituted phenyl)aziridin-2-yl phenyl ketone tosylhydrazones and *cis*-*N*-alkyl-3-phenylaziridin-2-yl 4-substituted phenyl ketone tosylhydrazones (3). To starting ketone (1a)(1.00 g, 3.76 mmol) in chloroform (50 ml) tosylhydrazine (2) (0.840 g, 3.76 mmolX1.2) was added under stirring. PPE-hydrolysate (3.00 g) was added to the mixture. The reaction was continued under room temperature until starting ketone (1) was not detected (1 h) on thin-layer chromatogram (silica gel, hexane/ethyl acetate (4:1)). The mixture was neutralized with 5 % aqueous sodium hydrogencarbonate. The chloroform layer

was washed three times with water, dried over anhydrous sodium sulfate, evaporated *in vacuo*. The residue crystallized from a small amount of methanol in a refrigerator and was purified from dichloromethane-methanol. The yield of 3a was 1.435 g (88 %). 3b-l were also prepared by the similar procedure.

Preparaton of 1-alkyl-6-phenyl-4-(4-substituted phenyl)-2-tosyl-1,2,5,6-tetrahydro-1,2,3-triazines and 1-alkyl-4-phenyl-6-(4-substituted phenyl)-2-tosyl-1,2,5,6-tetrahydro-1,2,3-triazines (8). To aziridinyl ketone tosylhydrazones (3a) (0.500 g, 1.15 mmol) in chloroform (15 ml) was added ethyl ether-boron trifluoride(1/1) (7) (0.229 g, 1.15 mmolX1.4) with stirring under room temperature. The reaction was continued under room temperature until 3a was not detected (3 h for 3a, 1-3 h for 3b-g, i-k) on thin-layer chromatogram (silica gel, hexane/ethyl acetate (4:1)). The mixture was neutralized with 5 % aqueous sodium hydrogencarbonate. The chloroform layer was washed three times with water, dried over anhydrous sodium sulfate, evaporated *in vacuo*. The residue crystallized from a small amount of methanol in a refrigerator and was purified from dichloromethane-methanol. The yield of 8a was 0.325 g (65 %). 8b-g, i-k were also prepared by the similar procedure.

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described in the literature for the preparation of 1b and used after identifing with nmr spectra.

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