REINVESTIGATION OF REACTION OF *CIS*-AZIRIDINYL KETONE SEMICARBAZONES AND TOSYLHYDRAZONES WITH DIETHYL ETHER-BORON TRIFLUORIDE(1/1)

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Abstract---A previously reported skeleton of reaction products of *cis*-1-alkyl-3-phenyl-aziridin-2-yl phenyl ketone semicarbazones (1) and tosyl hydrazones (2) with diethyl ether—boron trifluoride (1/1) was corrected to 2,3,4,5-tetrahydro-1,2,4-triazine derivatives (3) and (4), based on the results of reinvestigation with the X-Ray crystallography.

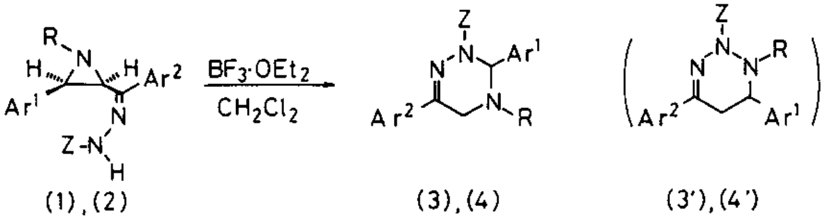
The Structure of 2,3,4,5-tetrahydro-1,2,4-triazine derivatives. Recently, we reported that 2-carbamoyl derivatives (**3'**)[1] and 2-tosyl (**4'**)[2] of 1-alkyl-4,6-diphenyl-1,2,5,6-tetrahydro-1,2,3-triazine were obtained in moderate yield *via* the rearrangement shown in Scheme 1. However, as a result of the X-Ray crystallography, it turned out that they were 2,3,4,5-tetrahydro-1,2,4-triazine derivatives (**3**) and (**4**) (Figure 1). C5 methylene in the structure (**3'** and **4'**) showed previously corresponds to that of **3** and **4**, and C6 methine of **3'** and **4'** to C3 methine of **3** and **4**. The IR, ^{1}H- and ^{13}C-NMR data presented in the previous papers[1,2] also supported the skeleton. Crystal of compound (**4b**) was grown by slow evaporation of methanol solutions at room temperature. The bond length between N1 and C6 was 1.300 Å and close to that of C=N double bond, comparing with those (1.28 Å) of oximes and imines reported in the literature.[3] The 1,2,4-triazine ring of **4b** was in the half-chair conformation and N2-N1-C6-C5 atoms were coplanar. Ar^1 on C3 and R on N4 were in an axial configuration because of mutual steric hindrance.

Experimental

Materials. *cis*-1-Alkyl-3-phenylaziridin-2-yl phenyl ketone semicarbazones

(1)[1] and tosylhydrazones (2),[2] 4-alkyl-2-carbamoyl-3,6-diphenyl-2,3,4,5-tetrahydro-1,2,4-triazines (3),[1] and 4-alkyl-3,6-diphenyl-2-tosyl-2,3,4,5-tetrahydro-1,2,4-triazines (4)[2] were prepared according to the method described previously.

NMR spectra of 3 and 4 ^{1}H-NMR data of 3 and 4 reported previously[1,2] were quoted in Tables 1 and 2.



Ar^1=p-X-C$_6$H$_4$
Ar^2=p-Y-C$_6$H$_4$

Z	
NH$_2$CO	(1) (3) (3')
Ts	(2) (4) (4')

	R	X	Y
a	i-Pr	H	H
b	c-C$_6$H$_{11}$	"	"
c	PhCH$_2$	"	"
d	t-Bu	"	"
e	c-C$_6$H$_{11}$	"	MeO
f	"	"	Me
g	"	"	Cl
h	"	MeO	H
i	"	Me	"
j	"	Cl	"

Scheme 1

X-Ray crystal structure determination of compound (4b). Crystals of compound **4b** were grown by slow evaporation of methanol solutions. A crystal of 0.2mm X 0.2 mm X 0.3 mm was mounted on a glass fiber on Rigaku AFC7R diffractometer with graphite monochromated Cu-Kα radiation and the lattice parameter were obtained by a least-squares refinement of 25 accurately centered reflections in the range 43.26°<2θ<53.77°. The structure was solved by direct methods using the SHELXS 86 suit of programs and conventional Fourier syntheses. The nonhydrogen atoms were refined anisotropically, and hydrogen atoms isotropically.

Crystal data $C_{28}H_{31}N_3O_2S$, M = 473.63, orthorhombic, space group Pbca(#61), a = 17.248(2) Å, b = 17.380(1) Å, c = 16.956(2) Å, V = 5082.9(8) Å^3, Z = 8, D_c = 1.238g·cm^{-3}, μ(CuKα) = 13.59 cm^{-1}, F_{000} = 2016.00

Data collection. *The data were collected at a temperature of 20±1 ℃ using* the ω-2θ scan technique to a maximum 2θ value of 120.1°. Scans of $(1.57 + 0.30\tan\theta)^\circ$ were made at a speed of $16.0^\circ \mathrm{min}^{-1}$(in omega). Number of data collected was 4242, number with $I \geqq 3.00\sigma(I)$ 1817.

Structure refinement.

$$R = \Sigma \| F_o | - | F_c \| / \Sigma | F_o | = 0.043$$

$$R_w = (\Sigma w (| F_o | - | F_c |)^2 / \Sigma w F_o^2)^{1/2} = 0.029$$

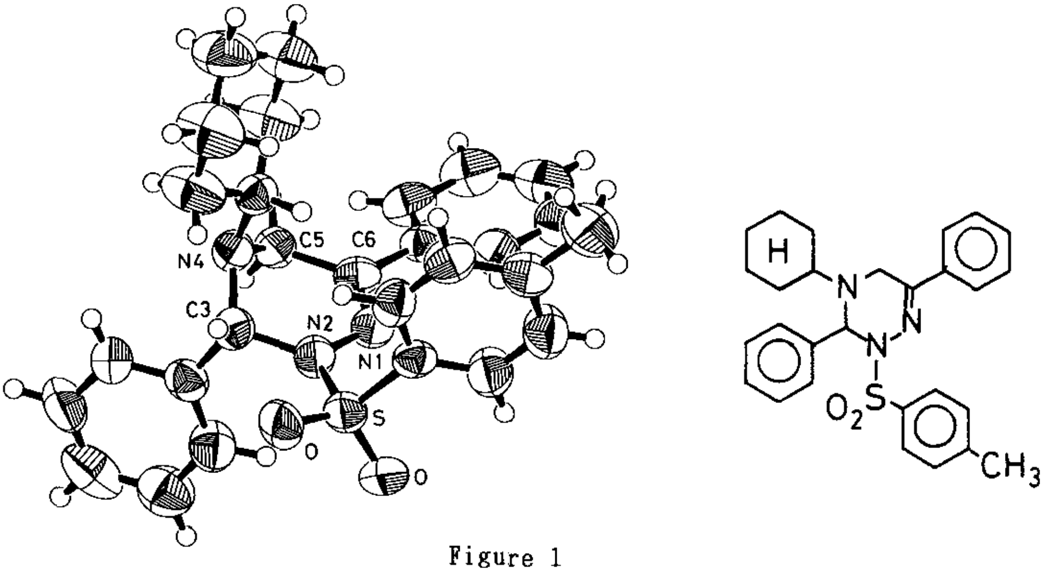


Figure 1

Table 1 ^{1}H-NMR data of compounds (3)

Compd	δ, *J* /Hz($CDCl_3$, TMS)
3a	1.18(3H,d,J=6.0,CH_3), 1.25(3H,d,J=6.0,CH_3), 3.04(1H,septet,J=6.0, i-propyl CH), 3.38(1H,d,J=18.7,CH_2), 3.72(1H,dd,J=18.7, 1.8,CH_2), 6.12 (2H,br s,NH_2), 6.54(1H,m*,CHPh), 7.10-7.64(10H,m,Ph)
3b	1.15-2.05(10H,m,c-hexyl CH_2), 2.56-2.80(1H,m,c-hexyl CH), 3.38(1H,d,J=18.4,CH_2), 3.74(1H,dd,J=18.4, 1.8,CH_2), 6.08(2H,br s,NH_2), 6.55(1H,m*, CHPh), 7.10-7.90(10H,m,Ph)
3c	3.45(2H,s,CH_2Ph), 3.70(1H,d,J=13.2,CH_2), 3.97(1H,d,J=13.2,CH_2), 5.01 (2H,br s,NH_2), 6.32(1H,s,CHPh), 7.23-7.70(15H,m,Ph)
3d	1.26(9H,s,CH_3), 3.38(1H,d,J=19.1,CH_2), 3.83(1H,dd,J=19.1, 2.4,CH_2), 5.66(2H,br s,NH_2), 6.76(1H,m*,CHPh)**, 7.10-7.65(10H,m,Ph)
3e	1.15-2.05(10H,m,c-hexyl CH_2), 2.60-2.67(1H,m,c-hexyl CH), 3.37(1H,d,J=18.6,CH_2), 3.68(1H,dd,J=18.6, 2.0,CH_2), 3.80(3H,s,OCH_3), 5.15(2H,br s,

	NH_2), 6.51(1H,m*,CHPh), 6.87-7.56(9H,m,Ph)
3f	1.15-2.04(10H,m,c-hexyl CH_2), 2.35(3H,s,CH_3), 2.61-2.66(1H,m,c-hexyl CH), 3.39(1H,d,J=18.6,CH_2), 3.68(1H,dd,J=18.6, 2.0,CH_2), 5.25(2H,br s, NH_2), 6.51(1H,m*,CHPh), 7.15-7.51(9H,m,Ph)
3g	1.16-2.03(10H,m,c-hexyl CH_2), 2.60-2.66(1H,m,c-hexyl CH), 3.39(1H,d,J=18.6,CH_2), 3.66(1H,dd,J=18.6, 1.5,CH_2), 5.35(2H,br s,NH_2), 6.52(1H,m*, CHPh), 7.22-7.53(9H,m,Ph)
3h	1.15-2.04(10H,m,c-hexyl CH_2), 2.60-2.66(1H,m,c-hexyl CH), 3.43(1H,d,J=18.6,CH_2), 3.70(1H,dd,J=18.6, 2.0,CH_2), 3.75(3H,s,OCH_3), 5.55(2H,br s, NH_2), 6.47(1H,m*,CHPh), 6.83-7.61(9H,m,Ph)
3i	1.15-2.04(10H,m,c-hexyl CH_2), 2.29(3H,s,CH_3), 2.60-2.65(1H,m,c-hexyl CH), 3.43(1H,d,J=18.6, CH_2), 3.70(1H,dd,J=18.6, 1.5, CH_2), 5.52(2H,br s, NH_2), 6.45(1H,m*,CHPh), 7.10-7.60(9H,m,Ph)
3j	1.15-2.02(10H,m,c-hexyl CH_2), 2.61-2.67(1H,m,c-hexyl CH), 3.38(1H,d,J=18.6,CH_2), 3.71(1H,dd,J=18.6, 1.5,CH_2), 5.52(2H,br s,NH_2), 6.48(1H,m*, CHPh), 7.23-7.60(9H,m,Ph)

* The coupling constants were not obtained on account of low resolution.

** The coupling of C3 benzyl protones with one of C5 methylene protones was confirmed with H-H COSY spectroscopy.

Table 2 ^{1}H-NMR data of compounds (4)

Compd	δ, J /Hz($CDCl_3$, TMS)
4a	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), 2.40-2.73(1H,septet,J=6.0,i-propyl CH), 3.21(1H,d,J=18.6,CH_2), 3.71(1H, dd,J=18.6, 2.0,CH_2), 6.33(1H,m*,CHPh), 7.10-8.00(14H,m,Ph)
4b	0.80-2.30(11H,m,c-hexyl), 2.43(3H,s,tolyl CH_3), 3.20(1H,d,J=18.0,CH_2), 3.75(1H,dd,J=18.0, 2.0,CH_2), 6.34(1H,m*,CHPh), 7.00-8.10(14H,m,Ph)
4c	2.43(3H,s,tolyl CH_3), 3.35(2H,s,CH_2Ph), 3.44(1H,d,J=17.2,CH_2), 3.68 (1H,dd,J=17.2, 2.0,CH_2), 6.04(1H,m*,CHPh), 7.00-8.10(19H,m,Ph)
4d	1.20(9H,s,t-butyl CH_3), 2.40(3H,s,tolyl CH_3), 3.19(1H,d,J=19.2,CH_2), 3.76(1H,dd,J=19.2, 2.0,CH_2), 6.55(1H,d,J=2.0,CHPh), 7.16-7.89(14H,m,Ph)
4e	0.80-2.30(11H,m,c-hexyl), 2.40(3H,s,tolyl CH_3), 3.12(1H,d,J=17.4,CH_2), 3.69(1H,dd,J=17.4, 1.8,CH_2), 3.78(3H,s,OCH_3), 6.27(1H,m*,CHPh), 6.80-7.91(13H,m, Ph)
4f	0.90-2.30(11H,m,c-hexyl), 2.31(3H,s,tolyl CH_3), 2.38(3H,s,tolyl CH_3), 3.13(1H,d,J=18.0,CH_2), 3.69(1H,dd,J=18.0, 1.8,CH_2), 6.24(1H,m*,CHPh), 7.09-7.91(13H,m,Ph)
4g	0.90-2.30(11H,m,c-hexyl), 2.42(3H,s,tolyl CH_3), 3.15(1H,d,J=18.0,CH_2), 3.66(1H,dd,J=18.0, 2.0,CH_2), 6.30(1H,m*,CHPh), 7.24-7.91(13H,m,Ph)
4h	0.90-2.30(11H,m,c-hexyl), 2.42(3H,s,tolyl CH_3), 3.21(1H,d,J=18.0,CH_2), 3.73(1H,dd,J=18.0, 2.0,CH_2), 3.78(3H,s,OCH_3), 6.26(1H,m*,CHPh),

	6.75-7.92(13H,m,Ph)
4i	0.90-2.30(11H,m,c-hexyl), 2.31(3H,s,tolyl CH_3), 2.41(3H,s,tolyl CH_3), 3.18(1H,d,J=18.0,CH_2), 3.70(1H,dd,J=18.0, 2.0,CH_2), 6.22(1H,m*,CHPh), 7.02-8.00(13H,m, Ph)
4j	0.90-2.20(11H,m,c-hexyl), 2.43(3H,s,tolyl CH_3), 3.13(1H,d,J=18.6,CH_2), 3.72(1H,dd,J=18.6, 2.0,CH_2), 6.25(1H,m*,CHPh), 7.26-7.92(13H,m,Ph)

* The coupling constants were not obtained on account of low resolution.

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