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-phenylaziridin-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') and 2-tosyl (4') 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, 1H- and 13C-NMR data presented in the previous papers1-3 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. Ar1 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)\textsuperscript{1} and tosylhydrazones (2),\textsuperscript{2} 4-alkyl-2-carbamoyl-3,6-diphenyl-2,3,4,5-tetrahydro-1,2,4-triazines (3),\textsuperscript{1} and 4-alkyl-3,6-diphenyl-2-tosyl-2,3,4,5-tetrahydro-1,2,4-triazines (4)\textsuperscript{2} were prepared according to the method described previously. NMR spectra of 3 and 4 \textsuperscript{1} were quoted in Tables 1 and 2.

\[ \text{[Scheme 1]} \]

X-Ray crystal structure determination of compound (4b). Crystals of compound 4b were grown by slow evaporation of methanol solutions. A crystal of 0.2 mm x 0.2 mm x 0.3 mm was mounted on a glass fiber on Rigaku AFC7R diffractometer with graphite monochromated Cu-K\textsubscript{α} radiation and the lattice parameter were obtained by a least-squares refinement of 25 accurately centered reflections in the range 43.26\textdegree<2θ<53.77\textdegree. 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\textsubscript{28}H\textsubscript{31}N\textsubscript{4}O\textsubscript{2}S, M = 473.63, orthorhombic, space group Pbc\textsubscript{a}(\#61), a = 17.248(2) Å, b = 17.380(1) Å, c = 16.956(2) Å, V = 5082.9(8) Å\textsuperscript{3}, Z = 8, D\textsubscript{c} = 1.238 g·cm\textsuperscript{-3}, \( \mu(\text{CuKα}) = 13.59 \text{ cm}^{-1} \), F\textsubscript{000} = 2016.00
Data collection. The data were collected at a temperature of 2021°C using the ω-2θ scan technique to a maximum 2θ value of 120.1°. Scans of (1.57 +0.30tanθ)° were made at a speed of 16.0°min⁻¹ (in omega). Number of data collected was 4242, number with I ≥ 3.00σ(I) 1817.

Structure refinement.

\[ R = \frac{\sum |F_o| - |F_c|}{\sum |F_o|} = 0.043 \]
\[ R_w = \left( \frac{\sum w (|F_o| - |F_c|)^2}{\sum w F_o^2} \right)^{1/2} = 0.029 \]

Figure 1

Table 1 ¹H-NMR data of compounds (3)

<table>
<thead>
<tr>
<th>Compd</th>
<th>( t, J ) /Hz(CDC13, TMS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>1.18(3H, d, J=6.0, CH₃), 1.25(3H, d, J=6.0, CH₃), 3.04(1H, septet, J=6.0, i-propyl CH), 3.38(1H, d, J=18.7, CH₂), 3.72(1H, dd, J=18.7, 1.8, CH₂), 6.12(2H, br s, NH₂), 6.54(1H, m, CHPh), 7.10-7.64(10H, m, Ph)</td>
</tr>
<tr>
<td>3b</td>
<td>1.15-2.05(10H, m, c-hexyl CH₂), 2.56-2.80(1H, m, c-hexyl CH), 3.38(1H, d, J=18.4, CH₂), 3.74(1H, dd, J=18.4, 1.8, CH₂), 6.08(2H, br s, NH₂), 6.55(1H, m, CHPh), 7.10-7.90(10H, m, Ph)</td>
</tr>
<tr>
<td>3c</td>
<td>3.45(2H, s, CH₂Ph), 3.70(1H, d, J=13.2, CH₂), 3.97(1H, d, J=13.2, CH₂), 5.01(2H, br s, NH₂), 6.32(1H, s, CHPh), 7.23-7.70(15H, m, Ph)</td>
</tr>
<tr>
<td>3d</td>
<td>1.26(9H, s, CH₃), 3.38(1H, d, J=19.1, CH₂), 3.83(1H, dd, J=19.1, 2.4, CH₂), 5.66(2H, br s, NH₂), 6.76(1H, m, CHPh)**, 7.10-7.65(10H, m, Ph)</td>
</tr>
<tr>
<td>3e</td>
<td>1.15-2.05(10H, m, c-hexyl CH₂), 2.60-2.67(1H, m, c-hexyl CH), 3.37(1H, d, J=18.6, CH₂), 3.68(1H, dd, J=18.6, 2.0, CH₂), 3.80(3H, s, OCH₃), 5.15(2H, br s,</td>
</tr>
</tbody>
</table>
NH₂), 6.51 (1H, m*, CHPh), 6.87-7.56 (9H, m, Ph)
3f 1.15-2.04 (10H, m, c-hexyl CH₂), 2.35 (3H, s, CH₃), 2.61-2.66 (1H, m, c-hexyl CH), 3.39 (1H, d, J=18.6, CH₂), 3.68 (1H, dd, J=18.6, 2.0, CH₂), 5.25 (2H, br s, NH₂), 6.51 (1H, m*, CHPh), 7.15-7.51 (9H, m, Ph)
3g 1.16-2.03 (10H, m, c-hexyl CH₂), 2.60-2.66 (1H, m, c-hexyl CH), 3.39 (1H, d, J=18.6, CH₂), 3.66 (1H, dd, J=18.6, 2.0, CH₂), 5.35 (2H, br s, NH₂), 6.52 (1H, m*, CHPh), 7.22-7.53 (9H, m, Ph)
3h 1.15-2.04 (10H, m, c-hexyl CH₂), 2.29 (3H, s, CH₃), 2.60-2.66 (1H, m, c-hexyl CH), 3.43 (1H, d, J=18.6, CH₂), 3.70 (1H, dd, J=18.6, 2.0, CH₂), 3.75 (3H, s, OCH₃), 5.55 (2H, br s, NH₂), 6.47 (1H, m*, CHPh), 7.10-7.60 (9H, m, Ph)
3i 1.15-2.04 (10H, m, c-hexyl CH₂), 2.61-2.67 (1H, m, c-hexyl CH), 3.44 (1H, d, J=18.6, CH₂), 3.71 (1H, dd, J=18.6, 2.0, CH₂), 5.52 (2H, br s, NH₂), 6.48 (1H, m*, CHPh), 7.23-7.60 (9H, m, Ph)
3j 1.15-2.02 (10H, m, c-hexyl CH₂), 2.61-2.67 (1H, m, c-hexyl CH), 3.44 (1H, d, J=18.6, CH₂), 3.72 (1H, dd, J=18.6, 2.0, CH₂), 5.52 (2H, br s, NH₂), 6.48 (1H, m*, CHPh)

* The coupling constants were not obtained on account of low resolution.
** The coupling of C3 benzyl protons with one of C5 methylene protons was confirmed with H-H COSY spectroscopy.

Table 2 ¹H-NMR data of compounds (4)

<table>
<thead>
<tr>
<th>Compd</th>
<th>δ, J /Hz(CDCl₃, TMS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4a</td>
<td>1.04 (3H, d, J=6.0, CH₃), 1.24 (3H, d, J=6.0, CH₃), 2.42 (3H, s, tolyl CH₃), 2.40-2.73 (1H, septet, J=6.0, 1-propyl CH), 3.21 (1H, d, J=18.6, CH₂), 3.71 (1H, dd, J=18.6, 2.0, CH₂), 6.33 (1H, m*, CHPh), 7.10-8.00 (14H, m, Ph)</td>
</tr>
<tr>
<td>4b</td>
<td>0.80-2.30 (11H, m, c-hexyl CH₂), 2.43 (3H, s, tolyl CH₃), 3.20 (1H, d, J=18.0, CH₂), 3.75 (1H, dd, J=18.0, 2.0, CH₂), 6.34 (1H, m*, CHPh), 7.00-8.10 (14H, m, Ph)</td>
</tr>
<tr>
<td>4c</td>
<td>2.43 (3H, s, tolyl CH₃), 3.35 (2H, s, CH₂Ph), 3.44 (1H, d, J=17.2, CH₂), 3.68 (1H, dd, J=17.2, 2.0, CH₂), 6.04 (1H, m*, CHPh), 7.00-8.10 (19H, m, Ph)</td>
</tr>
<tr>
<td>4d</td>
<td>1.20 (9H, s, t-butyl CH₂), 2.40 (3H, s, tolyl CH₃), 3.19 (1H, d, J=19.2, CH₂), 3.76 (1H, dd, J=19.2, 2.0, CH₂), 6.55 (1H, d, J=2.0, CHPh), 7.16-7.91 (13H, m, Ph)</td>
</tr>
<tr>
<td>4e</td>
<td>0.80-2.30 (11H, m, c-hexyl CH₂), 2.40 (3H, s, tolyl CH₃), 3.12 (1H, d, J=17.4, CH₂), 3.69 (1H, dd, J=17.4, 1.8, CH₂), 3.78 (3H, s, OCH₃), 6.27 (1H, m*, CHPh), 6.80-7.91 (13H, m, Ph)</td>
</tr>
<tr>
<td>4f</td>
<td>0.90-2.30 (11H, m, c-hexyl CH₂), 2.31 (3H, s, tolyl CH₃), 2.38 (3H, s, tolyl CH₃), 3.13 (1H, d, J=18.0, CH₂), 3.69 (1H, dd, J=18.0, 1.8, CH₂), 6.24 (1H, m*, CHPh), 7.09-7.91 (13H, m, Ph)</td>
</tr>
<tr>
<td>4g</td>
<td>0.90-2.30 (11H, m, c-hexyl CH₂), 2.42 (3H, s, tolyl CH₃), 3.15 (1H, d, J=18.0, CH₂), 3.66 (1H, dd, J=18.0, 2.0, CH₂), 6.30 (1H, m*, CHPh), 7.24-7.91 (13H, m, Ph)</td>
</tr>
<tr>
<td>4h</td>
<td>0.90-2.30 (11H, m, c-hexyl CH₂), 2.42 (3H, s, tolyl CH₃), 3.21 (1H, d, J=18.0, CH₂), 3.73 (1H, dd, J=18.0, 2.0, CH₂), 3.78 (3H, s, OCH₃), 6.26 (1H, m*, CHPh), 6.80-7.91 (13H, m, Ph)</td>
</tr>
</tbody>
</table>
6.75-7.92 (13H, m, Ph)

4i 0.90-2.30 (11H, m, c-hexyl), 2.31 (3H, s, tolyl CH₃), 2.41 (3H, s, tolyl CH₃),
   3.18 (1H, d, J=18.0, CH₂), 3.70 (1H, dd, J=18.0, 2.0, CH₂), 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 CH₃), 3.13 (1H, d, J=18.6, CH₂),
   3.72 (1H, dd, J=18.6, 2.0, CH₂), 6.25 (1H, m*, CHPh), 7.26-7.92 (13H, m, Ph)

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

REFERENCES
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Received, 9th December, 1997