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REDUCTION OF 3,4-DISUBSTITUTED 1,6-PROPANO-1H,6H-3a-THIA(S^{IV})-1,3,4,6-TETRAAZAPENTALENE-2,5(3H,4H)-DITHIONE WITH SODIUM BOROHYDRIDE

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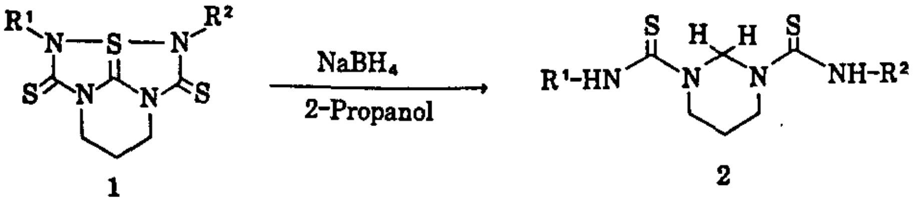
Abstract—— Reduction of tetraazapentalene derivatives with sodium borohydride ($NaBH_4$) afforded the ring-opening compound, 1,3-bis(substituted thiocarbamoyl)perhydropyrimidine, in good yields by the reduction-elimination of the $C=S^{IV}$ moiety.

We have recently reported the preparation of symmetrical tetraazapentalene derivatives (1a-c) by a convenient one-pot reaction using lithium thioureide/phenacyl chloride/alkyl isothiocyanate system,[1] the first example of the X-ray crystallographic structure[2] of a new heteropentalene, 3,4-diethyl-1,6-propano-1H,6H-3a-thia(S^{IV})-1,3,4,6-tetraazapentalene-2,5(3H,4H)-dithione (1b), and the smooth conversion of the symmetrical tetraazapentalene derivatives to the unsymmetrical tetraazapentalene derivatives (1d-g) via selective elimination, followed by 1,3-dipolar cycloaddition.[3] However, the reaction behavior of 1 has not been well investigated to date.[4] In our continuing study on the reaction behavior of tetraazapentalene derivatives, it was found that 1a-g reacts with reducing agents to give the ring-opening compound, 1,3-bis(substituted thiocarbamoyl)perhydropyrimidine, by the reduction-elimination of the $C=S^{IV}$ moiety. In this communication, we wish to report the regioselective reduction of symmetrical and unsymmetrical tetraazapentalene derivatives 1a-g with $NaBH_4$. 3,4-Dimethyl-1,6-propano-1H,6H-3a-thia(S^{IV})-1,3,4,6-tetraazapentalene-2,5(3H,4H)-dithione (1a) reacted with $NaBH_4$ in 2-propanol to give 1,3-bis(methyl thiocarbamoyl)perhydropyrimidine (2a) in good yields.[5] The evolution of hydrogen sulfide in this reaction was recognized. The yields and melting points of the reduction products 2a-g are shown in Table 1.



a: $R^1 = R^2 = CH_3$, b: $R^1 = R^2 = C_2H_5$, c: $R^1 = R^2 = CH_2{=}CHCH_2$
d: $R^1 = CH_3$, $R^2 = C_2H_5$, e: $R^1 = CH_3$, $R^2 = C_6H_5$, f: $R^1 = CH_3$, $R^2 = CH_2{=}CHCH_2$
g: $R^1 = C_2H_5$, $R^2 = CH_2{=}CHCH_2$

Table 1. Reduction of Tetraazapentalene Derivatives with $NaBH_4$*

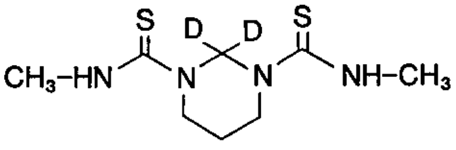
R^1	R^2	Solvent	Product	Mp/°C	Yield/%**
CH_3	CH_3	2-Propanol	<u>2a</u>	187-188	70 (24)***
CH_3	CH_3	Diglyme	<u>2a</u>	187-188	70
C_2H_5	C_2H_5	2-Propanol	<u>2b</u>	184-186	54
$CH_2{=}CHCH_2$	$CH_2{=}CHCH_2$	2-Propanol	<u>2c</u>	70-71	50
$CH_2{=}CHCH_2$	$CH_2{=}CHCH_2$	Diglyme	<u>2c</u>	70-71	54
CH_3	C_2H_5	2-Propanol	<u>2d</u>	161-162	84
CH_3	C_6H_5	2-Propanol	<u>2e</u>	146-147	51
CH_3	$CH_2{=}CHCH_2$	2-Propanol	<u>2f</u>	86-87	63
C_2H_5	$CH_2{=}CHCH_2$	2-Propanol	<u>2g</u>	61-63	73

* The reactions were carried out in 2-propanol at room temperature for 3 h.
** Isolated yield.
*** The reaction of <u>1a</u> with $LiAlH_4$ was carried out in ether at room temperature for 3 h.

The typical procedure for the reduction of tetraazapentalene derivatives with $NaBH_4$ is as follows: To a solution of <u>1a</u> (260 mg, 1.0 mmol) in 2-propanol (30 ml) was added 10 times molar quantity of $NaBH_4$, and the reaction mixture was stirred at room temperature for 3 h. After 2-propanol was evaporated, the residue was poured into water, and the mixture was extracted several times with chloroform. The chloroform layer was washed with water, dried over Na_2SO_4, and condensed under reduced pressure. Then the products were chromatographed on a preparative TLC (silica gel, dichloromethane:ethyl acetate = 4:1 as an eluent) to give <u>2a</u>.

Compound 2a was recrystallized from ethanol to give colorless solid (162 mg, 70%, mp 187-188 °C). This compound is stable under the atmosphere. All reduction products were characterized by spectroscopic data[6] and elemental analyses.

The reduction of 1a with sodium borodeuteride ($NaBD_4$) was performed in the same manner as with $NaBH_4$ to give the deuterated product (3a) in 70% yield. The structure of 3a was determined by the comparisons of spectral properties with those of 2a. In the ^1H nmr spectrum of 2a, the peak of the methylene protons at 2-position was observed at 5.6 ppm as a singlet, which disappeared in the ^1H nmr spectrum of 3a. The mass spectrum of 3a showed m/z 234 as a parent ion. These results indicate that regioselective attack of hydride ion took place at the carbon of 6a-position in 1a. Accordingly, the electronic structure of 1a is reasonably considered to be the reverse ylide one as shown in Figure 1.[7] Further studies are in progress on the reactivity of tetraazapentalene derivatives.



3a

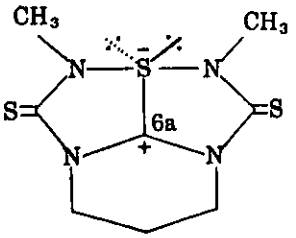


Figure 1

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3, N. Matsumura, M. Tomura, O. Mori, and S. Yoneda, Chem. Lett., 1987, 1065.

4, R. J. S. Beer and A. Naylor, Tetrahedron Lett., 1973, 2989; R. J. S. Beer, N. H. Holmes, and A. Naylor, J. Chem. Soc., Perkin Trans. I, 1979, 2909; R. J. S. Beer, H. Singh, D. Wright, and L. K. Hansen, Tetrahedron, 37, 2485 (1981).

5, Lithium aluminum hydride reacted with 1a in ether to give 2a in poor yield as one of many components (see Table 1). The reducing systems such as $NaBH_4$-$AlCl_3$, $NaBH_4$-$MgBr_2$, and $LiAlH_4$-$AlCl_3$ were examined for the reduction of 1a, but these systems were not good for the formation of 2a.

6, 2a: ^1H Nmr($CDCl_3$) δ = 1.80 (m, 2H, $NCH_2\underline{CH_2}CH_2N$), 3.15 (d, 6H, J=5.0Hz, $2xCH_3$), 4.00 (t, 4H, J=7.0Hz, $N\underline{CH_2}CH_2\underline{CH_2}N$), 5.60 (s, 2H, NCH_2N), and 7.00 (br, 2H, 2xNH); ^{13}C nmr($CDCl_3$) δ = 24.46, 32.64, 47.92, 62.38, and 182.43; ms m/z 232

(M^+); 2b: ^1H Nmr($CDCl_3$) δ = 1.25 (t, 6H, J=7.0Hz, $2xCH_2C\underline{H}_3$), 1.75 (m, 2H, $NCH_2C\underline{H}_2CH_2N$), 3.65 (d of q, 4H, J=4.0 and 7.0Hz, $2xC\underline{H}_2CH_3$), 3.95 (t, 4H, J=5.0Hz, $NC\underline{H}_2CH_2C\underline{H}_2N$), 5.55 (s, 2H, NCH_2N), and 6.85 (br, 2H, 2xNH); ms m/z 260 (M^+); 2c: ^1H Nmr($CDCl_3$) δ = 1.80 (m, 2H, $NCH_2C\underline{H}_2CH_2N$), 4.00 (t, 4H, J=6.0Hz, $NC\underline{H}_2CH_2C\underline{H}_2N$), 4.27 (m, 4H, $2xNC\underline{H}_2CH{=}CH_2$), 5.16-5.28 (m, 4H, $2xNCH_2CH{=}C\underline{H}_2$), 5.62 (s, 2H, NCH_2N), 5.86-6.00 (m, 2H, 2x $NCH_2C\underline{H}{=}CH_2$), and 7.18 (br, 2H, 2xNH); ^{13}C nmr($CDCl_3$) δ = 24.50, 48.03, 48.64, 62.51, 117.28, 133.28, and 181.43; ms m/z 284 (M^+); 2d: ^1H Nmr($CDCl_3$) δ = 1.27 (t, 3H, J=7.3Hz, $NHCH_2C\underline{H}_3$), 1.80 (m, 2H, $NCH_2C\underline{H}_2CH_2N$), 3.14 (d, 3H, J=4.3Hz, $NHCH_3$), 3.66 (d of q, 2H, J=4.9 and 7.4Hz, $NHC\underline{H}_2CH_3$), 3.98 (m, 4H, $NC\underline{H}_2CH_2C\underline{H}_2N$), 5.59 (s, 2H, NCH_2N), 6.92 (br, 1H, NH), and 7.10 (br, 1H, NH); ms m/z 246 (M^+); 2e: ^1H Nmr(DMSO-d_6) δ = 1.70 (m, 2H, $NCH_2C\underline{H}_2CH_2N$), 2.90 (s, 3H, CH_3), 3.85 (m, 4H, $NC\underline{H}_2CH_2C\underline{H}_2N$), 5.70 (s, 2H, NCH_2N), 7.20 (s, 5H, aromatic), 7.90 (br, 1H, NH), and 9.75 (br, 1H, NH); ms m/z 159 (M^+-PhNCS), and 135; 2f: ^1H Nmr($CDCl_3$) δ = 1.75 (m, 2H, $NCH_2C\underline{H}_2CH_2N$), 3.05 (d, 3H, J=6.0Hz, CH_3), 3.95 (t, 4H, J=5.0Hz, $NC\underline{H}_2CH_2C\underline{H}_2N$), 4.20 (m, 2H, $NC\underline{H}_2CH{=}CH_2$), 4.95-5.40 (m, 2H, $NCH_2CH{=}C\underline{H}_2$), 5.55 (s, 2H, NCH_2N), 5.60-6.30 (m, 1H, $NCH_2C\underline{H}{=}CH_2$), and 6.95-7.40 (br, 2H, 2xNH); ms m/z 258 (M^+); 2g: ^1H Nmr($CDCl_3$) δ = 1.35 (t, 3H, J=7.0Hz, $CH_2C\underline{H}_3$), 1.80 (m, 2H, $NCH_2C\underline{H}_2CH_2N$), 3.60 (d of q, 2H, J=5.0 and 7.0Hz, $C\underline{H}_2CH_3$), 3.95 (t, 4H, J=6.0Hz, $NC\underline{H}_2CH_2C\underline{H}_2N$), 4.20 (m, 2H, $NC\underline{H}_2CH{=}CH_2$), 5.00-5.40 (m, 2H, $NCH_2CH{=}C\underline{H}_2$), 5.55 (s, 2H, NCH_2N), 5.60-6.30 (m, 1H, $NCH_2C\underline{H}{=}CH_2$), and 6.80-7.30 (br, 2H, 2xNH); ms m/z 272 (M^+).
The microanalyses (C, H, and N) were in satisfactory agreement with the calculated value (within ± 0.3%).

7, Very recently, the bond-structure relationship of 6a-thia(S^{IV})pentalene analogs has been explained as shown in Figure 2. K. Akiba, Kagaku, 42, 539 (1987).

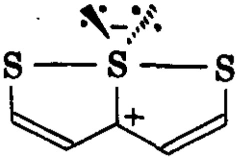

Figure 2

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