

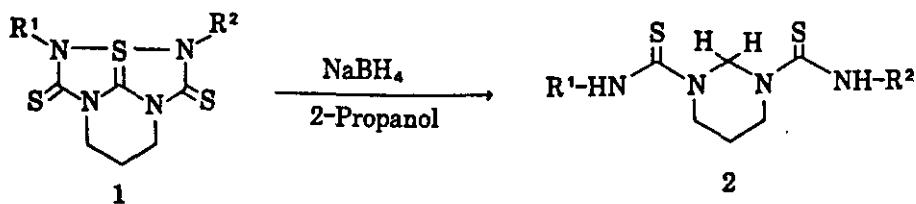
REDUCTION OF 3,4-DISUBSTITUTED 1,6-PROPANO-1H,6H-3a-THIA(S^{IV})-1,3,4,6-TETRAAZAPENTALENE-2,5(3H,4H)-DITHIONE WITH SODIUM BOROHYDRIDE

Noboru Matsumura,* Masaaki Tomura, Osamu Mori, Masataka Ukawa, and
Shigeo Yoneda*

Department of Applied Chemistry, College of Engineering,
University of Osaka Prefecture, Sakai, Osaka 591, Japan

Abstract— Reduction of tetraazapentalene derivatives with sodium borohydride (NaBH₄) 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 structure² 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 NaBH₄. 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 NaBH₄ 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: $\text{R}^1 = \text{R}^2 = \text{CH}_3$, b: $\text{R}^1 = \text{R}^2 = \text{C}_2\text{H}_5$, c: $\text{R}^1 = \text{R}^2 = \text{CH}_2=\text{CHCH}_2$
 d: $\text{R}^1 = \text{CH}_3$, $\text{R}^2 = \text{C}_2\text{H}_5$, e: $\text{R}^1 = \text{CH}_3$, $\text{R}^2 = \text{C}_6\text{H}_5$, f: $\text{R}^1 = \text{CH}_3$, $\text{R}^2 = \text{CH}_2=\text{CHCH}_2$
 g: $\text{R}^1 = \text{C}_2\text{H}_5$, $\text{R}^2 = \text{CH}_2=\text{CHCH}_2$

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
$\text{CH}_2=\text{CHCH}_2$	$\text{CH}_2=\text{CHCH}_2$	2-Propanol	<u>2c</u>	70-71	50
$\text{CH}_2=\text{CHCH}_2$	$\text{CH}_2=\text{CHCH}_2$	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	$\text{CH}_2=\text{CHCH}_2$	2-Propanol	<u>2f</u>	86-87	63
C_2H_5	$\text{CH}_2=\text{CHCH}_2$	2-Propanol	<u>2g</u>	61-63	73

* The reactions were carried out in 2-propanol at room temperature for 3 h.

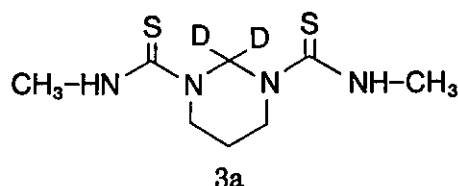
** Isolated yield.

*** The reaction of 1a 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 1a (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 2a.

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 data⁶ 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.

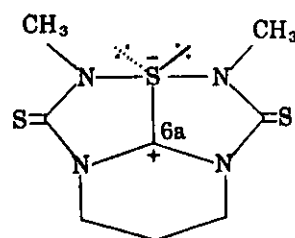


Figure 1

REFERENCES AND NOTES

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- 2, N. Matsumura, M. Tomura, S. Yoneda, and K. Toriumi, *Chem. Lett.*, **1986**, 1047.
- 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 $\text{NaBH}_4\text{-AlCl}_3$, $\text{NaBH}_4\text{-MgBr}_2$, and $\text{LiAlH}_4\text{-AlCl}_3$ 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, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$), 3.15 (d, 6H, $J=5.0\text{Hz}$, $2\times\text{CH}_3$), 4.00 (t, 4H, $J=7.0\text{Hz}$, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$), 5.60 (s, 2H, NCH_2N), and 7.00 (br, 2H, $2\times\text{NH}$); ^{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(CDCl₃) δ = 1.25 (t, 6H, J=7.0Hz, 2xCH₂CH₃), 1.75 (m, 2H, NCH₂CH₂CH₂N), 3.65 (d of q, 4H, J=4.0 and 7.0Hz, 2xCH₂CH₃), 3.95 (t, 4H, J=5.0Hz, NCH₂CH₂CH₂N), 5.55 (s, 2H, NCH₂N), and 6.85 (br, 2H, 2xNH); ms m/z 260 (M⁺); 2c: ¹H Nmr(CDCl₃) δ = 1.80 (m, 2H, NCH₂CH₂CH₂N), 4.00 (t, 4H, J=6.0Hz, NCH₂CH₂CH₂N), 4.27 (m, 4H, 2xNCH₂CH=CH₂), 5.16-5.28 (m, 4H, 2xNCH₂CH=CH₂), 5.62 (s, 2H, NCH₂N), 5.86-6.00 (m, 2H, 2x NCH₂CH=CH₂), and 7.18 (br, 2H, 2xNH); ¹³C nmr(CDCl₃) δ = 24.50, 48.03, 48.64, 62.51, 117.28, 133.28, and 181.43; ms m/z 284 (M⁺); 2d: ¹H Nmr(CDCl₃) δ = 1.27 (t, 3H, J=7.3Hz, NHCH₂CH₃), 1.80 (m, 2H, NCH₂CH₂CH₂N), 3.14 (d, 3H, J=4.3Hz, NHCH₃), 3.66 (d of q, 2H, J=4.9 and 7.4Hz, NHCH₂CH₃), 3.98 (m, 4H, NCH₂CH₂CH₂N), 5.59 (s, 2H, NCH₂N), 6.92 (br, 1H, NH), and 7.10 (br, 1H, NH); ms m/z 246 (M⁺); 2e: ¹H Nmr(DMSO-d₆) δ = 1.70 (m, 2H, NCH₂CH₂CH₂N), 2.90 (s, 3H, CH₃), 3.85 (m, 4H, NCH₂CH₂CH₂N), 5.70 (s, 2H, NCH₂N), 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(CDCl₃) δ = 1.75 (m, 2H, NCH₂CH₂CH₂N), 3.05 (d, 3H, J=6.0Hz, CH₃), 3.95 (t, 4H, J=5.0Hz, NCH₂CH₂CH₂N), 4.20 (m, 2H, NCH₂CH=CH₂), 4.95-5.40 (m, 2H, NCH₂CH=CH₂), 5.55 (s, 2H, NCH₂N), 5.60-6.30 (m, 1H, NCH₂CH=CH₂), and 6.95-7.40 (br, 2H, 2xNH); ms m/z 258 (M⁺); 2g: ¹H Nmr(CDCl₃) δ = 1.35 (t, 3H, J=7.0Hz, CH₂CH₃), 1.80 (m, 2H, NCH₂CH₂CH₂N), 3.60 (d of q, 2H, J=5.0 and 7.0Hz, CH₂CH₃), 3.95 (t, 4H, J=6.0Hz, NCH₂CH₂CH₂N), 4.20 (m, 2H, NCH₂CH=CH₂), 5.00-5.40 (m, 2H, NCH₂CH=CH₂), 5.55 (s, 2H, NCH₂N), 5.60-6.30 (m, 1H, NCH₂CH=CH₂), 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).

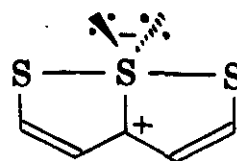


Figure 2

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