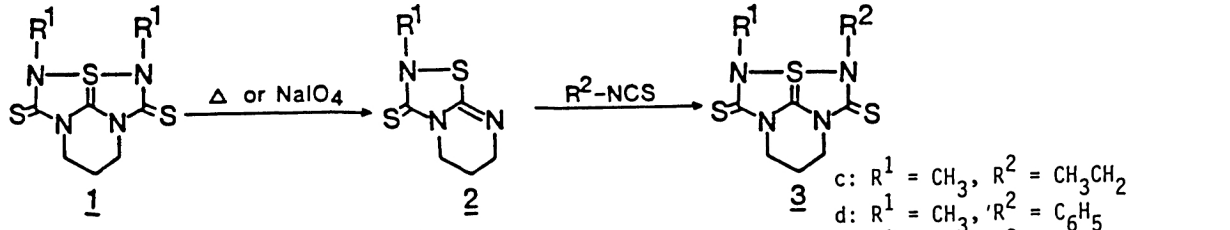
CHEMISTRY LETTERS, pp. 1065-1066, 1987.

Synthesis of Unsymmetrical Tetraazapentalene Derivatives

Noboru MATSUMURA,* Masaaki TOMURA, Osamu MORI, and Shigeo YONEDA*
Department of Applied Chemistry, College of Engineering,
University of Osaka Prefecture, Sakai, Osaka 591

The synthesis of unsymmetrical tetraazapentalene derivatives was achieved by the reaction of thiadiazole derivatives (2) with various isothiocyanates. Compounds 2 were easily derived from symmetrical tetraazapentalene derivatives.

We have recently reported the preparation of the tetraazapentalene derivatives by a convenient one-pot reaction using lithium thioureide/phenacyl chloride/alkyl isothiocyanate system.[1] These compounds are of interest from the structural point of view. In spite of the existence of four tertiary nitrogen atoms, the framework of (1) (R^1 = CH_3CH_2) was elucidated to be planar by X-ray crystallographic analysis.[2] This characteristic structure prompted us to investigate the chemical behavior of this type of tetraazapentalenes.



1
a: R^1 = CH_3
b: R^1 = CH_2=$CHCH_2$

2
a: R^1 = CH_3
b: R^1 = CH_2=$CHCH_2$

3
c: R^1 = CH_3, R^2 = CH_3CH_2
d: R^1 = CH_3, R^2 = C_6H_5
e: R^1 = CH_3, R^2 = p-ClC_6H_4
f: R^1 = CH_2=$CHCH_2$, R^2 = CH_3
g: R^1 = CH_2=$CHCH_2$, R^2 = CH_3CH_2
h: R^1 = CH_2=$CHCH_2$, R^2 = p-ClC_6H_4

The thermolysis or oxidation reaction of 3,4-dimethyl-1,6-propano-1H,6H-3a-thia(S^{IV})-1,3,4,6-tetraazapentalene-2,5(3H,4H)-dithione (1a) gave easily 6,7-dihydro-2-methyl-5H-pyrimido[1,2-d][1,2,4]thiadiazole-3(2H)-thione (2a). Furthermore, we have found that 2a undergoes a 1,3-dipolar cycloaddition with various isothiocyanates to give unsymmetrical tetraazapentalenes substituted by different groups at 3,4-positions. In this communication, we report the first preparation and characterization of various unsymmetrical tetraazapentalene derivatives.

When the compounds 1 were heated at 170 °C under reduced pressure (2 mmHg) or treated at room temperature with sodium metaperiodate in methanol, the products (2) were obtained in moderate yields. A typical procedure is as follows: Method A; Thermolysis of 1 (200 mg) was carried out at 170 °C for 5 h under reduced pressure (2 mmHg). Then the products were chromatographed on a preparative TLC to give 2 as a colorless solid. Method B; To a methanol solution of 1 (0.23 mmol) was added

a sodium metaperiodate (0.33 mmol) with stirring at room temperature under argon. After the reaction mixture was continued to stir for 5 h, methanol was removed in vacuo. The residual mixture was stirred in chloroform (50 ml) for 1 min, and the resulting suspension was filtered. After the filtrate was condensed under reduced pressure, the residue was chromatographed on a preparative TLC to give 2 as a colorless solid. The yields are shown in Table 1.

Table 1. Preparation of Thiadiazole Derivatives 2

	R^1	Method	Product	2, Yield/%
1a	CH_3	A[a)]	2a	69
1a	CH_3	B[b)]	2a	33
1b	CH_2=$CHCH_2$	A	2b	75
1b	CH_2=$CHCH_2$	B	2b	27

a) The compound was heated at 170 °C under reduced pressure.
b) Sodium metaperiodate was used as an oxidizing agent.

The thermolysis under reduced pressure (method A) is preferable to the oxidation reaction using $NaIO_4$ (method B) for the preparation of 2. The structure of 2 was determined by IR, ^{1}H-NMR, Mass spectra, and elemental analysis.

The compounds 2 reacted smoothly with the isothiocyanates to give (3). When the reactions of various isothiocyanates (1.5 times molar quantity of 2) with 2 were carried out in refluxing chloroform for 3 h, the unsymmetrical tetraazapentalene derivatives 3 were obtained in good yields. The yields and melting points are shown in Table 2. All compounds were characterized by IR, ^{1}H-NMR, ^{13}C-NMR, UV, Mass spectra, and elemental analyses.

Table 2. Preparation of Unsymmetrical Tetraazapentalene Derivatives 3[a)]

Entry	R^1	R^2	Product	Mp (dec.)/°C	Yield/%[b)]
1	CH_3	CH_3CH_2	3c	200-202	84
2	CH_3	C_6H_5	3d	179-182	85
3	CH_3	p-ClC_6H_4	3e	188-191	63
4	CH_2=$CHCH_2$	CH_3	3f	185-188	63
5	CH_2=$CHCH_2$	CH_3CH_2	3g	186-189	86
6	CH_2=$CHCH_2$	p-ClC_6H_4	3h	140-142	66

a) The reactions were carried out in refluxing chloroform for 3 h.
b) Isolated yield.

References

1) N. Matsumura, M. Tomura, R. Mando, Y. Tsuchiya, and S. Yoneda, Bull. Chem. Soc. Jpn., 59, 3693 (1986); N. Matsumura, M. Tomura, Y. Tsuchiya, S. Yoneda, and M. Nakamura, Chem. Express, 1, 487 (1986).
2) N. Matsumura, M. Tomura, S. Yoneda, and K. Toriumi, Chem. Lett., 1986, 1047.

(Received February 21, 1987)