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# Synthesis of Unsymmetrical Tetraazapentalene Derivatives

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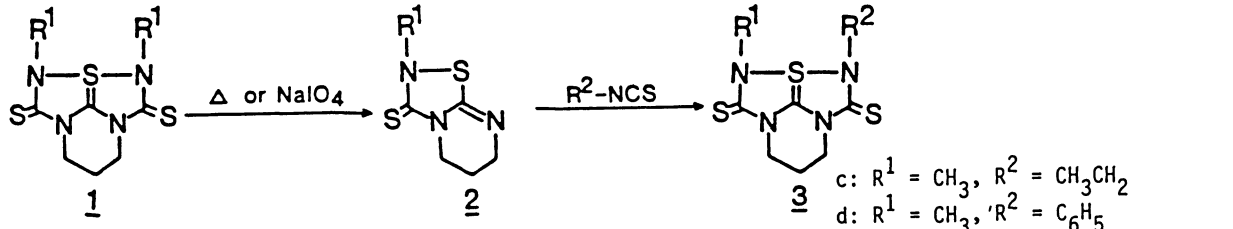
The synthesis of unsymmetrical tetraazapentalene derivatives was achieved by the reaction of thiadiazole derivatives (2) with various isothiocyanates. Compounds 2 were easily derived from symmetrical tetraazapentalene derivatives.

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

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2) N. Matsumura, M. Tomura, S. Yoneda, and K. Toriumi, Chem. Lett., 1986, 1047.

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