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Synthesis of Novel Tetraazapentalene Derivatives (10-S-3) with a Hypervalent Sulfur and Carbonyl Groups

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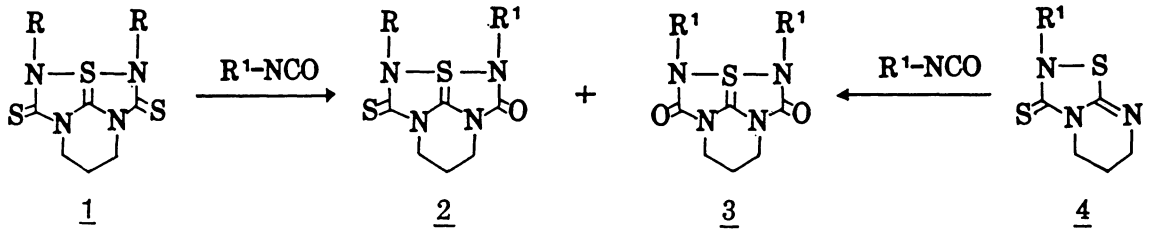
Tetraazapentalenes (R = CH_3 and CH_2=$CHCH_2$) reacted with isocyanates to give new types of tetraazapentalenes, (2) and (3). The compounds, 2 and 3, were also obtained by the reaction of isocyanates with thiadiazolopyrimidines.

In the previous paper,[1] we have reported that tetraazapentalenes, 6,7-dihydro-2,3-disubstituted 5H-2a-thia(2a-S^{IV})-2,3,4a,7a-tetraazacyclopent[cd]indene-1,4(2H,3H)-dithione (1), are prepared by a convenient one-pot reaction using the lithium thioureide/phenacyl chloride/alkyl isothiocyanate system. However, tetraazapentalenes (3) with two carbonyl groups were not obtained by the similar synthetic method using alkyl isocyanate. During the course of our study on the reactivity of tetraazapentalenes, we have found that 1a reacts with methyl isocyanate to give new tetraazapentalene derivatives (2a and 3a) by the replacement of the isothiocyanate moiety in 1a by methyl isocyanate. The compounds, 2a and 3a,



1

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

2

a: R = R^1 = CH_3
b: R = CH_3, R^1 = C_6H_5
c: R = CH_3, R^1 = $ClCH_2CH_2$
d: R = CH_3, R^1 = CH_2=C(-CH_3)-$COOCH_2CH_2$
e: R = CH_2=$CHCH_2$, R^1 = CH_3
f: R = CH_2=$CHCH_2$, R^1 = C_6H_5
g: R = CH_2=$CHCH_2$, R^1 = $ClCH_2CH_2$
h: R = CH_2=$CHCH_2$, R^1 = CH_2=C(-CH_3)-$COOCH_2CH_2$

3

a: R^1 = CH_3
b: R^1 = C_6H_5
c: R^1 = $ClCH_2CH_2$
d: R^1 = CH_2=C(-CH_3)-$COOCH_2CH_2$

4

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

Scheme 1.

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also were obtained by the reaction of methyl isocyanate with 6,7-dihydro-2-methyl-5H-1,2,4-thiadiazolo[4,5-a]pyrimidine-3(2H)-thione (4a) which was readily derived from 1a by the thermolysis or oxidation reaction.[2] The preparation and reactivity of tetraazapentalenes, 2 and 3, have not been well investigated so far.[3]

In this communication, we wish to report a facile synthesis of the novel tetraazapentalene derivatives with the carbonyl groups using the reaction of 1 and 4 with various isocyanates (Scheme 1).

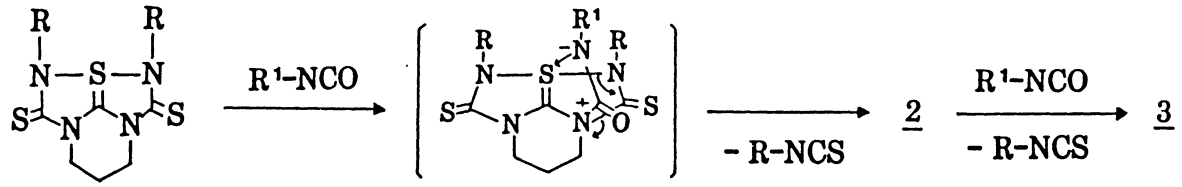
When the reactions of 1 and 4 with various isocyanates were carried out under reflux in chloroform, the products, 2 and 3, were obtained in relatively good yields. A typical procedure is described for the preparation of tetraazapentalenes, 2 and 3: To a solution of 1a (83 mg, 0.32 mmol) in chloroform (30 ml) was added methyl isocyanate (182 mg, 3.2 mmol) with stirring at room temperature. After the reaction mixture was refluxed for 6 h, the solvent was evaporated. The residue was chromatographed on a preparative TLC (silica gel, ethyl acetate as an eluent) to give 2a (Rf 0.4, 25 mg, 32%) and 3a (Rf 0.1, 19 mg, 26%) as colorless solids.

Table 1. Reaction of Tetraazapentalenes 1 with Isocyanates[a]

Entry	Tetraazapentalene	R^1-NCO R^1	Time/h	2[b]	Yield/%[c]	3[b]	Yield/%[c]
1	1a	CH_3	6	2a	32	3a	26
2	1a	C_6H_5	6	2b	53	3b	30
3	1a	$ClCH_2CH_2$	6	2c	32	3c	21
4	1a	$CH_2=C(CH_3)-COOCH_2CH_2$	24	2d	10	3d	73
5	1b	CH_3	6	2e	-	3a	78
6	1b	C_6H_5	6	2f	55	3b	35
7	1b	$ClCH_2CH_2$	6	2g	-	3c	78
8	1b	$CH_2=C(CH_3)-COOCH_2CH_2$	24	2h	8	3d	68

a) Reactions of 1 with various isocyanates were carried out under reflux in chloroform. Molar ratio of 1 to R^1-NCO = 1 : 10. b) Structure of the products was assigned on the basis of IR, ^1H NMR, and MS spectra as well as elemental analyses. c) Yield of isolated product. The yields are based on 1.

The structure of 2a-h and 3a-d was determined by IR, ^1H NMR,[4] mass spectra, and elemental analysis. Table 1 shows the results in the reactions of 1a and 1b with various isocyanates. As shown in Table 1, the yields of tetraazapentalenes, 2 and 3, depended on the kinds of alkyl groups of alkyl isocyanate and 1. Generally, the yields of 3 from 1b were better than those from 1a. The plausible reaction mechanism is outlined in Scheme 2.



Scheme 2.

Next, the reactions of isocyanates with thiadiazolopyrimidine derivatives, 4a and 4b, were carried out under the similar conditions. Consequently, tetraazapentalenes, 2 and 3, were obtained in moderate yields as shown in Table 2. The reaction is explained to proceed by the 1,3-dipolar cycloaddition of R^1-N=C=O to the S-C=N moiety in 4, followed by the transformation of 2 into 3.

Table 2. Reaction of Thiadiazolopyrimidines 4 with Isocyanates[a)]

Entry	Thiadiazolo-pyrimidine	R^1-NCO R^1	Time/h	2[b)]	Yield/%[c)]	3[b)]	Yield/%[c)]
1	4a	CH_3	6	2a	13	3a	34
2	4a	C_6H_5	6	2b	31	3b	24
3	4a	$ClCH_2CH_2$	6	2c	43	3c	52
4	4a	$CH_2=\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}-COOCH_2CH_2$	24	2d	-	3d	98
5	4b	CH_3	6	2e	31	3a	50
6	4b	C_6H_5	6	2f	24	3b	69
7	4b	$ClCH_2CH_2$	6	2g	16	3c	84
8	4b	$CH_2=\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}-COOCH_2CH_2$	24	2h	-	3d	81

a) Reactions of 1 with various isocyanates were carried out under reflux in chloroform. Molar ratio of 4 to R^1-NCO = 1 : 10. b) Structure of all products was assigned on the basis of IR, ^1H NMR, and MS spectral data and elemental analyses. c) Isolated product. The yields are based on 4.

Further studies on the reactivity of the novel tetraazapentalenes, 2 and 3, with the functional groups are now in progress.

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

3) R. J. S. Beer, N. H. Holmes, and A. Naylor, J. Chem. Soc., Perkin Trans. 1, 1979, 2909.

4) 2a: ^{1}H NMR($CDCl_3$) δ = 2.29(m, 2H, $NCH_2C\underline{H}_2CH_2N$), 2.95(s, 3H, NCH_3), 3.19(s, 3H, NCH_3), 3.99(t, 2H, J=5.8 Hz, $NC\underline{H}_2CH_2CH_2N$), and 4.38(t, 2H, J=5.8 Hz, $NCH_2CH_2C\underline{H}_2N$); 2b: ^{1}H NMR($CDCl_3$) δ = 2.24(m, 2H, $NCH_2C\underline{H}_2CH_2N$), 3.20(s, 3H, NCH_3), 3.98(t, 2H, J=5.8 Hz, $NC\underline{H}_2CH_2CH_2N$), 4.27(t, 2H, J=5.8 Hz, $NCH_2CH_2C\underline{H}_2N$), and 7.12-7.41(m, 5H, aromatic); 2c: ^{1}H NMR($CDCl_3$) δ = 2.31(m, 2H, $NCH_2C\underline{H}_2CH_2N$), 3.21(s, 3H, NCH_3), 3.68(s, 4H, $NC\underline{H}_2C\underline{H}_2Cl$), 4.00(t, 2H, J=5.8 Hz, $NC\underline{H}_2CH_2CH_2N$), and 4.37(t, 2H, J=5.8 Hz, $NCH_2CH_2C\underline{H}_2N$); 2d: ^{1}H NMR($CDCl_3$) δ = 1.95(m, 3H, $COC(C\underline{H}_3)=CH_2$), 2.31(m, 2H, $NCH_2C\underline{H}_2CH_2N$), 3.16(s, 3H, NCH_3), 3.67(t, 2H, J=5.2 Hz, $NC\underline{H}_2CH_2OCO$), 3.99(t, 2H, J=5.8 Hz, $NC\underline{H}_2CH_2CH_2N$), 4.27(t, 2H, J=5.5 Hz, $NCH_2CH_2C\underline{H}_2N$), 4.37(t, 2H, J=5.8 Hz, $NCH_2C\underline{H}_2OCO$), 5.60(m, 1H, $CH_3C=C\underline{\overset{H}{H}}$), and 6.16(m, 1H, $CH_3C=C\underline{\overset{H}{H}}$); 2e: ^{1}H NMR($CDCl_3$) δ = 2.30(m, 2H, $NCH_2C\underline{H}_2CH_2N$), 2.94(s, 3H, NCH_3), 3.99(t, 2H, J=5.8 Hz, $NC\underline{H}_2CH_2CH_2N$), 4.33(m, 2H, $NC\underline{H}_2CH=CH_2$), 4.39(t, 2H, J=5.8 Hz, $NCH_2CH_2C\underline{H}_2N$), 5.21-5.26(m, 2H, $NCH_2CH=C\underline{H}_2$), and 5.95-6.04(m, 1H, $NCH_2C\underline{H}=CH_2$); 2f: ^{1}H NMR($CDCl_3$) δ = 2.35(m, 2H, $NCH_2C\underline{H}_2CH_2N$), 4.08(t, 2H, J=5.8 Hz, $NC\underline{H}_2CH_2CH_2N$), 4.36-4.40(m, 4H, $NCH_2CH_2C\underline{H}_2N$ and $NC\underline{H}_2CH=CH_2$), 5.23-5.30(m, 2H, $NCH_2CH=C\underline{H}_2$), 5.94-6.02(m, 1H, $NCH_2C\underline{H}=CH_2$), and 7.14-7.45(m, 5H, aromatic); 2g: ^{1}H NMR($CDCl_3$) δ = 2.32(m, 2H, $NCH_2C\underline{H}_2CH_2N$), 3.67(s, 4H, $NC\underline{H}_2C\underline{H}_2Cl$), 4.00(t, 2H, J=5.8 Hz, $NC\underline{H}_2CH_2CH_2N$), 4.34-4.44(m, 4H, $NCH_2CH_2C\underline{H}_2N$ and $NC\underline{H}_2CH=CH_2$), 5.24-5.28(m, 2H, $NCH_2CH=C\underline{H}_2$), and 5.91-6.04(m, 1H, $NCH_2C\underline{H}=CH_2$); 2h: ^{1}H NMR($CDCl_3$) δ = 1.94(m, 3H, $OCOC(C\underline{H}_3)=CH_2$), 2.31(m, 2H, $NCH_2C\underline{H}_2CH_2N$), 3.66(t, 2H, J=5.2 Hz, $NC\underline{H}_2CH_2CH_2N$), 4.00(t, 2H, J=5.8 Hz, $NCH_2CH_2C\underline{H}_2N$), 4.26-4.44(m, 6H, $NC\underline{H}_2CH=CH_2$ and $NC\underline{H}_2C\underline{H}_2OCO$), 5.16-5.22(m, 2H, $NCH_2CH=C\underline{H}_2$), 5.58(m, 1H, $CH_3C=C\underline{\overset{H}{H}}$), 5.85-5,99(m, 1H, $NCH_2C\underline{H}=CH_2$), and 6.15(m, 1H, $CH_3C=C\underline{\overset{H}{H}}$); 3a: ^{1}H NMR($CDCl_3$) δ = 2.23(m, 2H, $NCH_2C\underline{H}_2CH_2N$), 2.90(s, 6H, 2 x NCH_3), and 3.94(t, 4H, J=5.5 Hz, $NC\underline{H}_2CH_2CH_2N$); 3b: ^{1}H NMR($CDCl_3$) δ = 2.35(m, 2H, $NCH_2C\underline{H}_2CH_2N$), 4.07(t, 4H, J=5.8 Hz, $NC\underline{H}_2CH_2CH_2N$), and 7.15-7.45(m, 10H, aromatic); 3c: ^{1}H NMR($CDCl_3$) δ = 2.27(m, 2H, $NCH_2C\underline{H}_2CH_2N$), 3.67(s, 8H, 2 x $NC\underline{H}_2C\underline{H}_2Cl$), and 3.97(t, 4H, J=6.1 Hz, $NC\underline{H}_2CH_2CH_2N$); 3d: ^{1}H NMR($CDCl_3$) δ = 1.95(s, 6H, 2 x $C(C\underline{H}_3)=CH_2$), 2.26(m, 2H, $NCH_2C\underline{H}_2CH_2N$), 3.61(t, 4H, J=5.5 Hz, 2 x $NC\underline{H}_2CH_2OCO$), 3.96(t, 4H, J=5.9 Hz, $NC\underline{H}_2CH_2C\underline{H}_2N$), 4.24(t, 4H, J=5.5 Hz, 2 x $NCH_2C\underline{H}_2OCO$), 5.60(m, 2H, 2 x $CH_3C=C\underline{\overset{H}{H}}$), and 6.16(m, 2H, 2 x $CH_3C=C\underline{\overset{H}{H}}$).

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