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Synthesis of Novel Tetraazapentalene Derivatives with Fused Cyclic Systems

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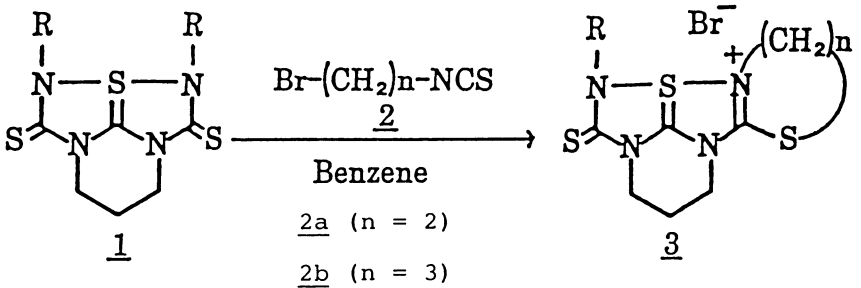
Tetraazapentalene derivatives (R = CH_3, CH_2=$CHCH_2$) reacted with ω-halogenoalkyl isothiocyanates to give novel tetraazapentalene derivatives with fused cyclic systems in good yields.

Recently we have reported the synthesis[1] and the reactivity[2] of tetraazapentalene derivative, 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). During the course of our study on the reactivity of tetraazapentalenes, we have found that 1a reacts with 2-bromoethyl isothiocyanate to give 1,2,5,6-tetrahydro-8-methyl-4H-3,8a-dithia(8a-S^{IV})-3b,6a,8-triaza-8b-azoniacyclopenta[a]cyclopent[cd]indene-7(8H)-thione bromide (3a). We now wish to report on the synthesis of novel tetraazapentalene derivatives with fused cyclic systems by the reactions of 1 with ω-halogenoalkyl isothiocyanates.



1

3

a: R = CH_3

b: R = CH_2=$CHCH_2$

a: R = CH_3; n = 2

b: R = CH_2=$CHCH_2$; n = 2

c: R = CH_3; n = 3

d: R = CH_2=$CHCH_2$; n = 3

ω-Bromoalkyl isothiocyanates (2) were prepared from the corresponding ω-bromoalkyl amine hydrobromide and thiophosgene according to the method described in the literature.[3] A typical procedure for the reaction of 1 with 2 is as follows: 2-Bromoethyl isothiocyanate (133 mg, 0.8 mmol) was added to a solution of 1a (104 mg, 0.4 mmol) in benzene (20 ml) with stirring at room temperature. The mixture was refluxed under argon for 2 h. The resulting precipitate was filtered off and recrystallized from ethyl alcohol to yield 119 mg (84%) of 3a. The

filtrate was concentrated in vacuo. The residue was chromatographed on silica gel with dichloromethane to give trace amounts of 1a. 3a: Mp 237-238 °C (decomp); IR(KBr) 2930, 1610, 1560, 1490, 1340, 1270, 1210, 1150, 1050, and 950 cm^{-1}; ^1H NMR(CD_3OD) δ = 2.52 (m, 2H, $NCH_2C\underline{H}_2CH_2N$), 3.54 (s, 3H, NCH_3), 3.96 (t, 2H, $SC\underline{H}_2CH_2N$, J = 8.1 Hz), 4.27 (t, 2H, $NC\underline{H}_2CH_2CH_2N$, J = 6.0 Hz), 4.38 (t, 2H, $NCH_2CH_2C\underline{H}_2N$, J = 6.0 Hz), and 4.46 (t, 2H, $SCH_2C\underline{H}_2N$, J = 8.1 Hz); ^{13}C NMR(CD_3OD) δ = 20.63, 34.80, 38.94, 48.34, 50.33, 58.90, 165.19, 165.49, and 174.75. Found: C, 30.37; H, 3.62; N, 15.60%. Calcd for $C_9H_{13}N_4S_3Br$: C, 30.59; H, 3.71; N, 15.85%. Table 1 shows the yields of the products 3a-d in the reaction of 1 with 2.

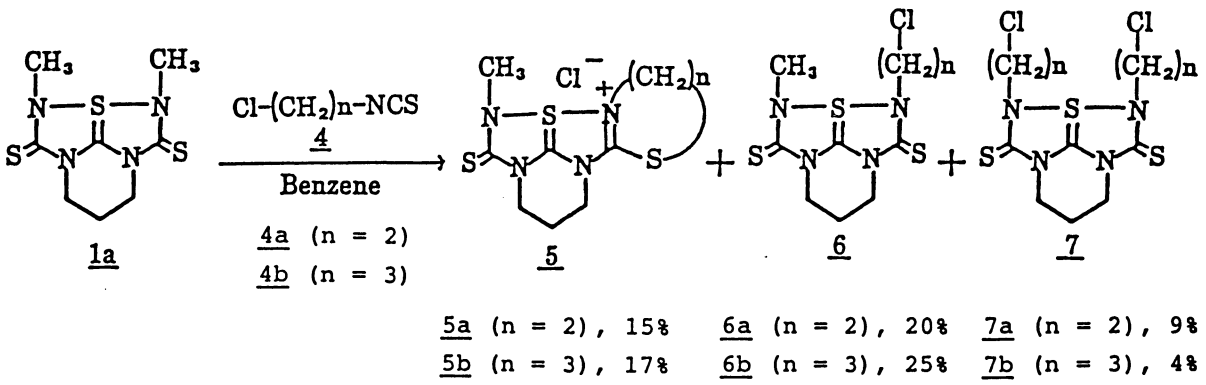
Table 1. The reactions of Tetraazapentalene Derivatives 1a and 1b with ω-Bromoalkyl Isothiocyanates 2[a)]

Tetraazapentalene	ω-Bromoalkyl isothiocyanate	Product	Yield/%[b)]
1a	$BrCH_2CH_2NCS$ (2a)	3a	84
1a	$BrCH_2CH_2CH_2NCS$ (2b)	3c	86
1b	$BrCH_2CH_2NCS$ (2a)	3b	97
1b	$BrCH_2CH_2CH_2NCS$ (2b)	3d	95

a) The reactions were carried out in benzene under reflux for 2 h.
b) Isolated yields were based on 1.

As shown in Table 1, the products 3a-d were obtained in high yields without the formation of tetraazapentalene fused with two rings. Furthermore, the S-alkylated tetraazapentalene with the $-(CH_2)_nNCS$ group also was not obtained.

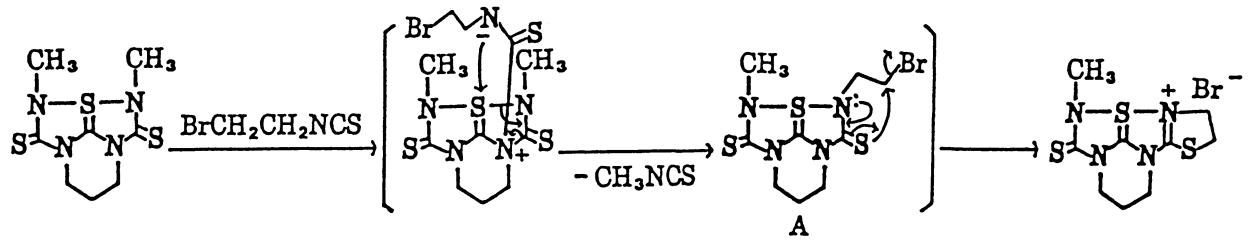
Next, the reaction of 1a with ω-chloroalkyl isothiocyanates (4)[3)] was carried out under similar conditions described above. The results are shown in Scheme 1.



Scheme 1.

In this reaction, the yield of tetraazapentalene (5) with fused ring decreased

remarkably, and mono- and di-N-chloroalkyltetraazapentalenes (6) and (7) were formed as other products. Thus, the yields of tetraazapentalene derivatives with fused ring were affected by the kinds of the halogen atom of ω-halogenoalkyl isothiocyanate used. In addition, we have found that the tetraazapentalene 6a is converted to 5a in benzene under reflux for 60 h in 33% yield. Furthermore, the ^{1}H NMR spectrum of 1a in bromobenzene-d_5 at 80.1 °C indicated that methyl isothiocyanate is not eliminated from 1a. From the above results, the plausible reaction mechanism is outlined in Scheme 2. The reaction is explained to proceed by the replacement of the isothiocyanate moiety of 1a by 2-bromoethyl isothiocyanate to form an intermediate A, followed by the intramolecular cyclization shown in Scheme 2.



Scheme 2.

The structure of all products in the reactions described above was determined by IR, ^{1}H NMR,[4] ^{13}C NMR, Mass spectra, and elemental analysis.

Further studies on the reactivity of tetraazapentalene derivatives, 3a-d, are now in progress.

References

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2) N. Matsumura, M. Tomura, O. Mori, and S. Yoneda, Chem. Express, 2, 421 (1987); N. Matsumura, O. Mori, M. Tomura, and S. Yoneda, ibid., 2, 631 (1987); N. Matsumura, M. Tomura, O. Mori, M. Ukawa, and S. Yoneda, Heterocycles, 1987, 3097; N. Matsumura, M. Tomura, O. Mori, Y. Takamura, and S. Yoneda, Tetrahedron Lett., in press.

3) P. Friis, Acta Chem. Scand., 19, 766 (1965).

4) 3b: ^{1}H NMR($CDCl_3$) δ = 2.59 (m, 2H, $NCH_2CH_2CH_2N$), 3.86 (t, 2H, SCH_2CH_2N, J =

8.0 Hz), 4.43 (t, 2H, $SCH_2C\underline{H}_2N$, J = 8.0 Hz), 4.54-4.64 (m, 6H, $NC\underline{H}_2CH_2C\underline{H}_2N$ and $NC\underline{H}_2CH=CH_2$), 5.43-5.49 (m, 2H, $NCH_2CH=C\underline{H}_2$), and 5.94-6.02 (m, 1H, $NCH_2C\underline{H}=CH_2$); 3c: ^1H NMR($CDCl_3$) δ = 2.25 (m, 2H, $SCH_2C\underline{H}_2CH_2N$), 2.58 (m, 2H, $NCH_2C\underline{H}_2CH_2N$), 3.40 (s, 3H, NCH_3), 3.41 (t, 2H, $SC\underline{H}_2CH_2CH_2N$, J = 6.0 Hz), 3.97 (t, 2H, $SCH_2CH_2C\underline{H}_2N$, J = 6.0 Hz), 4.47 (t, 2H, $NC\underline{H}_2CH_2CH_2N$, J = 6.0 Hz), and 4.55 (t, 2H, $NCH_2CH_2C\underline{H}_2N$, J = 6.0 Hz); 3d: ^1H NMR($CDCl_3$) δ = 2.23 (m, 2H, $SCH_2C\underline{H}_2CH_2N$), 2.58 (m, 2H, $NCH_2C\underline{H}_2CH_2N$), 3.47 (t, 2H, $SC\underline{H}_2CH_2CH_2N$, J = 6.0 Hz), 3.95 (t, 2H, $SCH_2CH_2C\underline{H}_2N$, J = 6.0 Hz), 4.47-4.59 (m, 6H, $NC\underline{H}_2CH_2C\underline{H}_2N$ and $NC\underline{H}_2CH=CH_2$), 5.37-5.40 (m, 2H, $NCH_2CH=C\underline{H}_2$), and 5.92-6.00 (m, 1H, $NCH_2C\underline{H}=CH_2$); 5a: ^1H NMR(CD_3OD) δ = 2.47 (m, 2H, $NCH_2C\underline{H}_2CH_2N$), 3.50 (s, 3H, NCH_3), 3.91 (t, 2H, $SC\underline{H}_2CH_2N$, J = 8.0 Hz), 4.22 (t, 2H, $NC\underline{H}_2CH_2CH_2N$, J = 6.0 Hz), 4.33 (t, 2H, $NCH_2CH_2C\underline{H}_2N$, J = 6.0 Hz), and 4.42 (t, 2H, $SCH_2C\underline{H}_2N$, J = 8.0 Hz); 5b: ^1H NMR(CD_3OD) δ = 2.16 (m, 2H, $SCH_2C\underline{H}_2CH_2N$), 2.46 (m, 2H, $NCH_2C\underline{H}_2CH_2N$), 3.38 (s, 3H, NCH_3), 3.44 (t, 2H, $SC\underline{H}_2CH_2CH_2N$, J = 6.0 Hz), 3.94 (t, 2H, $SCH_2CH_2C\underline{H}_2N$, J = 6.0 Hz), 4.20 (t, 2H, $NC\underline{H}_2CH_2CH_2N$, J = 5.5 Hz), and 4.36 (t, 2H, $NCH_2CH_2C\underline{H}_2N$, J = 5.5 Hz); 6a: ^1H NMR(CD_3OD) δ = 2.38 (m, 2H, $NCH_2C\underline{H}_2CH_2N$), 3.26 (s, 3H, NCH_3), 3.84 (t, 2H, $NC\underline{H}_2CH_2Cl$, J = 6.0 Hz), 4.03 (t, 2H, $NCH_2C\underline{H}_2Cl$, J = 6.0 Hz), and 4.42-4.45 (m, 4H, $NC\underline{H}_2CH_2C\underline{H}_2N$); 6b: ^1H NMR($CDCl_3$) δ = 2.24 (m, 2H, $NCH_2C\underline{H}_2CH_2Cl$), 2.37 (m, 2H, $NCH_2C\underline{H}_2CH_2N$), 3.25 (s, 3H, NCH_3), 3.60 (t, 2H, $NC\underline{H}_2CH_2CH_2Cl$, J = 6.0 Hz), 3.89 (t, 2H, $NCH_2CH_2C\underline{H}_2Cl$, J = 6.0 Hz), and 4.41 (m, 4H, $NC\underline{H}_2CH_2C\underline{H}_2N$); 7a: ^1H NMR(CD_3OD) δ = 2.40 (m, 2H, $NCH_2C\underline{H}_2CH_2N$), 3.85 (t, 4H, $NC\underline{H}_2CH_2Cl$, J = 5.5 Hz), 4.06 (t, 4H, $NCH_2C\underline{H}_2Cl$, J = 5.5 Hz), and 4.42 (t, 4H, $NC\underline{H}_2CH_2C\underline{H}_2N$, J = 6.0 Hz); 7b: ^1H NMR($CDCl_3$) δ = 2.25 (m, 4H, $NCH_2C\underline{H}_2CH_2Cl$), 2.38 (m, 2H, $NCH_2C\underline{H}_2CH_2N$), 3.60 (t, 4H, $NC\underline{H}_2CH_2CH_2Cl$, J = 6.5 Hz), 3.89 (t, 4H, $NCH_2CH_2C\underline{H}_2Cl$, J = 6.5 Hz), and 4.41 (t, 4H, $NC\underline{H}_2CH_2C\underline{H}_2N$, J = 6.0 Hz).

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