CHEMISTRY LETTERS, pp. 2141-2144, 1992.

Reaction of Tetraazapentalene Derivatives Having Fused Cyclic Systems with the I_2/NH_4OH Reagent

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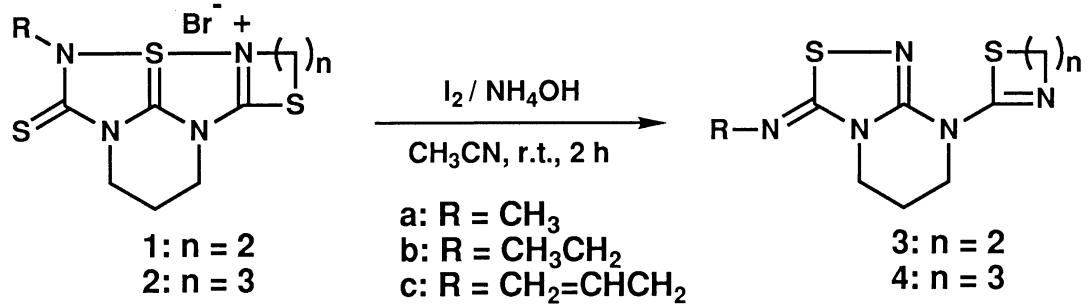
Tetraazapentalene derivatives having fused cyclic systems reacted with the I_2/NH_4OH reagent to give 1,2,4-thiadiazolo[4,3-*a*]pyrimidine derivatives with the release of the hypervalent sulfur. The molecular structure of the product was determined by the X-ray crystallographic analysis.

Recently we have reported that tetraazapentalene derivatives (**1** and **2**) having fused cyclic systems[1] are synthesized by the reaction of 6,7-dihydro-2,3-disubstituted 5*H*-2a-thia(2*a*-S^{IV})-2,3,4a,7a-tetraazacyclopent[*cd*]indene-1,4(2*H*,3*H*)-dithione[2] with ω-bromoalkyl isothiocyanates. It is expected that the novel cations **1** and **2** with a hypervalent sulfur show various chemical behavior toward nucleophilic reagents.[3] During the course of our study on the reactivity of **1** and **2**, we have found that **1** and **2** react with the I_2/NH_4OH reagent, which is used for a ring expansion of heteroaromatic cations,[4] to give 1,2,4-thiadiazolo[4,3-*a*]pyrimidine derivatives (**3** and **4**), respectively, not ring expansion products. In this communication, we describe the details of the reactions of tetraazapentalene cations **1** and **2** with the I_2/NH_4OH reagent, the spectral characterization of the products **3** and **4**, and the X-ray crystallographic analysis of **3a**.



A typical procedure for the reaction of tetraazapentalene cations **1** and **2** with the I_2/NH_4OH reagent is as follows: To an acetonitrile solution (10 ml) of **1a** (100 mg, 0.283 mmol) were added aqueous ammonia (28%, 10 ml) and an acetonitrile solution (10 ml) of iodine (144 mg, 0.566 mmol) at room temperature. After stirring under the same conditions for 2 h, the mixture was poured into water (100 ml). The solution was extracted with

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dichloromethane. The extract was washed with water, dried over Na_2SO_4, and condensed in vacuo. Column chromatography or TLC of the residue on silica gel using dichloromethane : ethyl acetate = 4 : 1 (v/v) as an eluent gave 49 mg (68%) of **3a** as a colorless solid. Recrystallization from hexane-chloroform afforded a pure sample. Table 1 shows the yields and the melting points of the products **3a-c** and **4a-c** in the reactions of **1a-c** and **2a-c** with the I_2/NH_4OH reagent. The IR, ^1H NMR,[5] ^{13}C NMR, and Mass spectral data and the results of elemental analysis[6] of all products are consistent with the assignment of the 8-(substituted imino)-1,2,4-thiadiazolo[4,3-*a*]pyrimidine structure.

Table 1. The Yields and the Melting Points of the Products **3a-c** and **4a-c**

Products	R	Yield/%[a]	Melting point/°C
3a	CH_3	68	156 - 158
3b	CH_3CH_2	65	63 - 64
3c	CH_2=$CHCH_2$	68	102 - 103
4a	CH_3	60	91 - 92
4b	CH_3CH_2	67	88 - 89
4c	CH_2=$CHCH_2$	66	oil

a) Isolated yields were based on **1** and **2**.

All reactions gave the 8-(substituted imino)-1,2,4-thiadiazolo[4,3-*a*]pyrimidine derivatives **3** and **4** in moderate yields with the release of the hypervalent sulfur of **1** and **2**, whereas no ring expansion products were obtained. The reaction at the C=N$^+$ moiety of **1** and **2** did not occur at all. The results are consistent with those in the reduction of **1** and **2** using sodium borohydride[3] and the treatment of **1** and **2** with acid.[7] In the absence of iodine, the reaction did not give the 1,2,4-thiadiazolo[4,3-*a*]pyrimidine derivatives **3** and **4**, but a complex mixture containing a small amount of 1,3-disubstituted perhydropyrimidin-2-one derivatives[7] was obtained.

In order to determine the structure of the products, the X-ray crystallographic analysis of **3a** was carried out.[8] Figure 1 shows an ORTEP II[9] drawing of compound **3a**. The X-ray analysis shows that the products

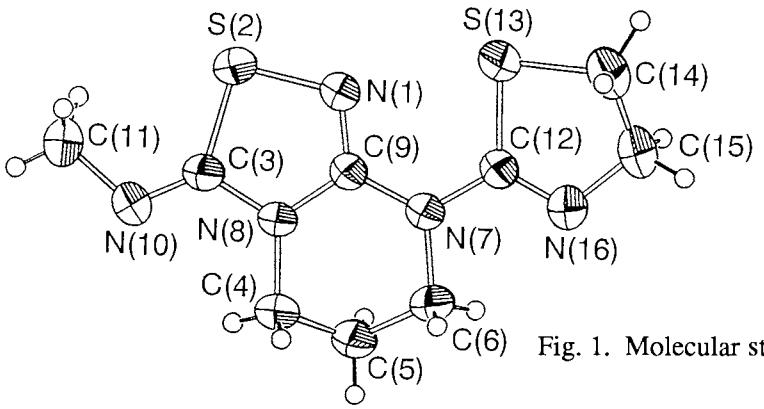
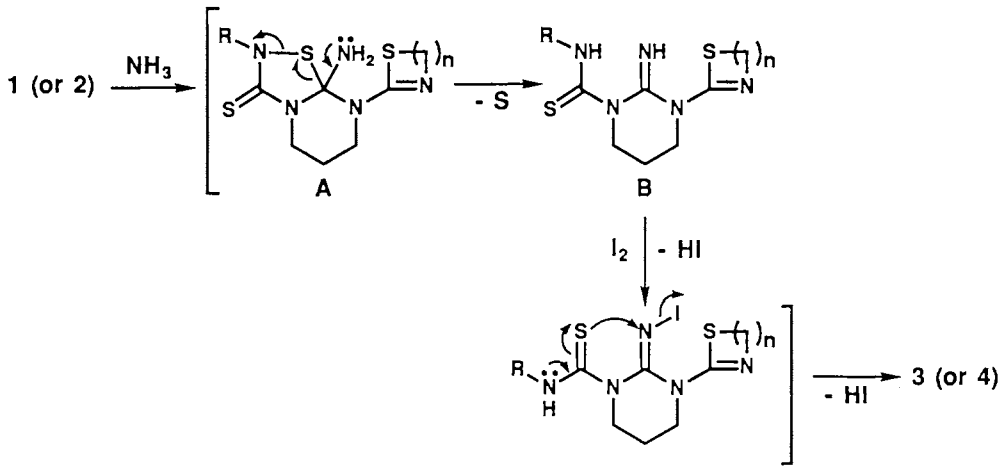


Fig. 1. Molecular structure of the compound **3a**.

have the 8-(substituted imino)-1,2,4-thiadiazolo[4,3-*a*]pyrimidine structure. It was found that the 1,2,4-thiadiazole ring containing N(10), C(4), N(7), and C(6) and the 4,5-dihydrothiazole ring except C(14) are nearly planar.

Although the detailed mechanism is unclear at present, it is speculated that the reaction is initiated by a nucleophilic attack of ammonia on the $C=S^{IV}$ carbon of **1** and **2**, followed by the cleavage of the hypervalent S^{IV}-N^{+} bond to form the intermediate (**A**). The elimination of the sulfur atom from **A**[10] gives the guanidine intermediate (**B**) which undergoes ring-closure by oxidation with I_2[4] to afford the product **3** or **4**. However, the eliminated sulfur could not be identified.



Further studies on the reactivity of the tetraazapentalene derivatives **1** and **2** having fused cyclic systems are now in progress.

References

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5) **3a**: ^{1}H NMR($CDCl_3$) δ = 2.13 (m, 2H, $NCH_2C\underline{H}_2CH_2N$), 2.99 (s, 3H, CH_3), 3.29 (t, 2H, $NCH_2C\underline{H}_2S$, J = 8.1 Hz), 3.75 (t, 2H, $NC\underline{H}_2CH_2CH_2N$, J = 6.7 Hz), and 4.01 - 4.06 (m, 4H, $NCH_2CH_2C\underline{H}_2N$ and $NC\underline{H}_2CH_2S$); **3b**: ^{1}H NMR($CDCl_3$) δ = 1.26 (t, 3H, $C\underline{H}_3CH_2$, J = 7.3 Hz), 2.11 (m, 2H, $NCH_2C\underline{H}_2CH_2N$), 3.07 (q, 2H, $CH_3C\underline{H}_2$, J = 7.3 Hz), 3.26 (t, 2H, $NCH_2C\underline{H}_2S$, J = 8.0 Hz), 3.80 (t, 2H, $NC\underline{H}_2CH_2CH_2N$, J = 6.1 Hz), and 4.01 - 4.06 (m, 4H, $NCH_2CH_2C\underline{H}_2N$ and $NC\underline{H}_2CH_2S$); **3c**: ^{1}H NMR($CDCl_3$) δ = 2.13 (m, 2H, $NCH_2C\underline{H}_2CH_2N$), 3.28 (t, 2H, $NCH_2C\underline{H}_2S$, J = 7.9 Hz), 3.70 (d of t, 2H, CH_2=$CHC\underline{H}_2N$, J = 6.1 and 1.2 Hz), 3.81 (t, 2H, $NC\underline{H}_2CH_2CH_2N$, J = 6.7 Hz), 4.00 - 4.05 (m, 4H, $NCH_2CH_2C\underline{H}_2N$ and $NC\underline{H}_2CH_2S$), 5.10 - 5.31 (m, 2H, $C\underline{H}_2$=$CHCH_2N$), and 5.93 - 6.03 (m, 1H, CH_2=$C\underline{H}CH_2N$); **4a**: ^{1}H NMR($CDCl_3$) δ = 1.89 (m, 2H, $NCH_2C\underline{H}_2CH_2S$), 2.10 (m, 2H, $NCH_2C\underline{H}_2CH_2N$), 2.98 (s, 3H, CH_3), 3.04 (t, 2H, $NCH_2CH_2C\underline{H}_2S$, J = 6.1 Hz), 3.71 (t, 2H, $NC\underline{H}_2CH_2CH_2N$), and 3.72 - 3.80 (m, 4H, $NCH_2CH_2C\underline{H}_2N$ and $NC\underline{H}_2CH_2CH_2S$); **4b**: ^{1}H NMR($CDCl_3$) δ = 1.23 (t, 3H, $C\underline{H}_3CH_2$, J = 6.9 Hz), 1.89 (m, 2H, $NCH_2C\underline{H}_2CH_2S$), 2.10 (m, 2H,

$NCH_2C\underline{H}_2CH_2N$), 3.01 - 3.13 (m, 4H, $NCH_2CH_2C\underline{H}_2S$ and $CH_3C\underline{H}_2$), and 3.71 - 3.81 (m, 6H, $NC\underline{H}_2CH_2C\underline{H}_2N$ and $NC\underline{H}_2CH_2CH_2S$); **4c**: ^1H NMR($CDCl_3$) δ = 1.89 (m, 2H, $NCH_2C\underline{H}_2CH_2S$), 2.10 (m, 2H, $NCH_2C\underline{H}_2CH_2N$), 3.04 (t, 2H, $NCH_2CH_2C\underline{H}_2S$), 3.69 - 3.81 (m, 8H, $NC\underline{H}_2CH_2C\underline{H}_2N$, $NC\underline{H}_2CH_2CH_2S$, and CH_2=$CHC\underline{H}_2N$), 5.10 - 5.30 (m, 2H, $C\underline{H}_2$=$CHCH_2N$), and 5.91 - 6.04 (m, 1H, CH_2=$C\underline{H}CH_2N$).

6) The molecular formula of **4c** was determined by the exact MS data: Exact MS m/z 295.0943 (M^+). Calcd for $C_{12}H_{17}N_5S_2$: 295.0926.

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8) Crystal data for **3a**: $C_8H_{13}N_5S_2$, F_w = 241.34, monoclinic, space group $P2_1/n$, a = 18.558(2), b = 7.4894(6), c = 18.550(2) Å, β = 115.677(8)°, V = 2323.6(4) $Å^3$, T = 297 K, F(000) = 1008, Z = 8, Dx = 1.380 gcm^{-3}, μ(Mo-Kα) = 0.42 mm^{-1}. The crystal had approximate dimensions of 0.47 × 0.30 × 0.1 mm. Data were collected on a Rigaku AFC-5R diffractometer (λ = 0.71069 Å). 5818 reflections were obtained in the range of $2<2\theta<55°$ by the ω-2θ technique at a 2θ rate of 8° min^{-1} and the scan width $\Delta\omega$ = $(1.3+0.4\tan\theta)°$. Usual Lorentz and polarization corrections were applied and absorption effect was applied numerically. 3611 observed data were used for refinement ($F>3\sigma(F)$). The structure was solved by direct method using SHELXS86[11] and successive Fourier syntheses and refined by the block-diagonal least-square using UNICS III[12] with anisotropic temperature factors for non-H atoms and isotropic ones for H. Σ $w(|Fc|-k^{-1}|Fo|)^2$ was minimized, $w = 1/[\sigma^2(F)+0.36693|Fo|-0.00057|Fo|^2]$, to give R = 0.060, R_w = 0.091. Atomic scattering factors were taken from those of International Tables for X-ray Crystallography.[13] Computations were performed on an IBM ES/3090-180S of the Information Processing Center of the University of Electro-Communications.

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(Received July 15, 1992)