Photoinduced Electron Transfer Reaction of Tetraazathiapentalenes with Trialkylamines

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The photoinduced electron transfer reaction of tetraazathiapentalenes with trialkylamines gives thiourea derivatives by dialkylamination of isothiocyanate derivatives, through radical anions of tetraazathiapentalenes and radical cations of trialkylamines.

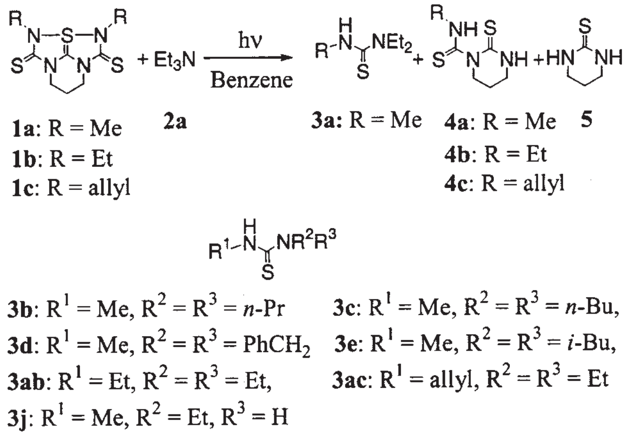
Recently, much attention has been focused on the characteristic properties and reactivities of hypervalent compounds having 3-center of 4-electron bond.[1] However, little is known about the photoinduced electron transfer reaction of these compounds. We have previously reported the formation of charge transfer (CT)-complex between tetraazathiapentalene derivative (**1a**) bearing hypervalent sulfur and tetracyanoquinodimethane (TCNQ), where **1a** serves as an electron donating molecule.[2] We now report a novel photoinduced electron transfer reaction of **1a–c** with trialkylamines to give thiourea derivatives, where **1a–c** serve as electron accepting molecules. Although several α-diethylaminoethylation and ethylation by use of triethylamine (**2a**) have been reported previously,[3–5] to the best of our knowledge, there is no example about diethylamination via photoinduced electron transfer.

Irradiation of a benzene solution containing **1a** (1 mM) and a large excess of triethylamine (**2a**) through Pyrex filter ($\lambda > 280$ nm) under Ar atmosphere gave N,N-diethyl-N′-methylthiourea (**3a**) in a 73% isolated yield accompanying **4a**, **5**, and acetaldehyde. The structures of these products were determined by their spectral properties and by direct comparison with those of authentic samples.

Similar irradiation of **1a** with trialkylamines such as tripropylamine (**2b**), tributylamine (**2c**), and tribenzylamine (**2d**) afforded the corresponding dialkylaminated products **3b–d**, respectively. Triisobutylamine (**2e**) also gave the diisobutylaminated product **3e**, but the yield was low. In addition, the photoreaction of **1b–c** with **2a** afforded the corresponding diethylaminated thiourea derivatives (**3ab** and **3ac**). Similar irradiation of **1a** with diethylamine (**2i**) in benzene afforded **3a**, but **2i** is less reactive than **2a**. The photoreaction did not occur in the case of ethylamine (**2j**). In the cases of aromatic amines (**2f–h**), the photoreaction did not proceed or gave a complex mixture. These results are summarized in Table 1.

From the mechanistic viewpoints, the effects of solvents and additives were examined. The photoreaction also proceeded smoothly in CH_3CN and CH_3OH, to give **3**, **4**, and **5** in good yields (Entry 2–3). The photoreaction of **1a** with **2a** was not sensitized by triplet sensitizers such as benzophenone and Michler's ketone. However, interestingly, 1,4-dimethoxynaphthalene (DMN) sensitized the photoreaction of **1a** with **2j** to give N-ethyl-N′-methylthiourea (**3j**).

In the dark overnight, **1a** and **2a** were completely recovered even under reflux conditions. The formation of **3a** can be reasonably explained by the reaction of diethylamine and methyl isothiocyanate. In fact, diethylamine efficiently reacts with methyl isothiocyanate at ambient temperature in the dark, although both of them were not detected in the photoreaction mixture of **1a** and **2a**. In addition, the photoreaction of **1a** in the absence of **2a** in benzene did not produce any product at all and **1a** was recovered quantitatively.



1a: R = Me
1b: R = Et
1c: R = allyl
2a
3a: R = Me
4a: R = Me
4b: R = Et
4c: R = allyl
5

3b: R^1 = Me, R^2 = R^3 = *n*-Pr
3c: R^1 = Me, R^2 = R^3 = *n*-Bu,
3d: R^1 = Me, R^2 = R^3 = $PhCH_2$
3e: R^1 = Me, R^2 = R^3 = *i*-Bu,
3ab: R^1 = Et, R^2 = R^3 = Et,
3ac: R^1 = allyl, R^2 = R^3 = Et
3j: R^1 = Me, R^2 = Et, R^3 = H

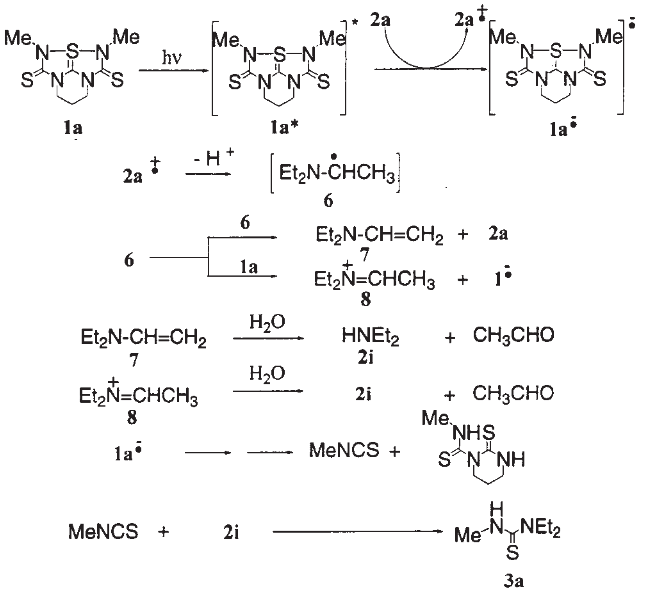
Scheme 1.

Table 1. Photoinduced electron transfer reaction of tetraazathiapentalene derivatives (**1a–c**) with amines (**2a–j**)[a]

Entry	1	Amine	Product yields/%[b] 3	4	5
1	**1a**	Et_3N (**2a**)	**3a** (73)	**4a** (trace)	(41)
2[c]	**1a**	**2a**	**3a** (64)	**4a** (50)	trace
3[d]	**1a**	**2a**	**3a** (81)	**4a** (68)	trace
4	**1a**	*n*-Pr_3N (**2b**)	**3b** (94)	**4a** (trace)	trace
5	**1a**	*n*-Bu_3N (**2c**)	**3c** (92)	**4a** (trace)	trace
6	**1a**	$(PhCH_2)_3N$ (**2d**)	**3d** (93)	**4a** (trace)	trace
7	**1a**	*i*-Bu_3N (**2e**)	**3e** (40)	—[e]	—[e]
8	**1a**	Ph_3N (**2f**)	(0)	(0)	(0)
9[f]	**1a**	dimethylaniline (**2g**)	—	—	—
10	**1a**	diethylaniline (**2h**)	(0)	**4a** (0)	(0)
11	**1b**	**2a**	**3ab** (37)	—[e]	—[e]
12	**1c**	**2a**	**3ac** (50)	—[e]	—[e]
13	**1a**	Et_2NH (**2i**)	**3a** (60)	—[e]	—[e]
14	**1a**	$EtNH_2$ (**2j**)	**3j** (0)	**4a** (0)	(0)
15[g]	**1a**	**2j**	**3j** (16)	—[e]	—[e]

[a]Reaction conditions; $[\mathbf{1a}] = 1.0 \times 10^{-3}$ M $[\mathbf{2a}] = 0.1$ M. Irradn time; 24 h through Pyrex filter (>280 nm) in benzene. [b]Isolated yields. [c]In CH_3CN. [d]In CH_3CN-MeOH (1 : 99). [e]Not determined. [f]A complex mixture was obtained. [g]1,4-Dimethoxynaphthalene (DMN) was added as a sensitizer.

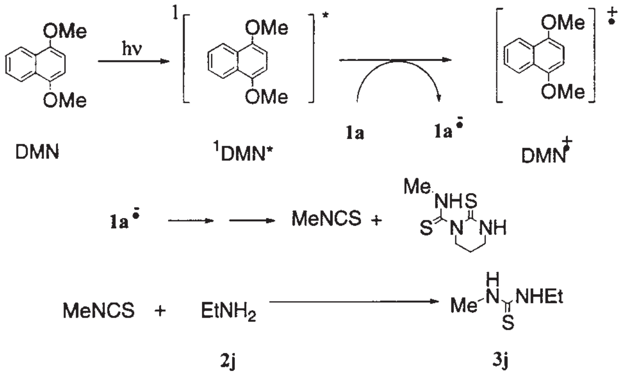
On the basis of these results, we propose the mechanism for the formation of **3a** as shown in Scheme 2. The first step is the photoinduced electron transfer from **2a** to the excited singlet state of **1a** to form the radical cation of **2a** ($\mathbf{2a}^{+\bullet}$) and the radical anion of **1a** ($\mathbf{1a}^{-\bullet}$). The single electron transfer reaction mechanism from amines to **1a*** is supported by the facts that the tertiary and secondary amines are susceptible to the dialkylamination, but primary amine is not. The second step is an elimination of a proton on α-carbon of $\mathbf{2a}^{+\bullet}$ to give the radical (**6**). This radical **6** may produce an enamine (**7**) or an iminium cation (**8**) by disproportionation of **6** or one-electron oxidation by **1a**, as suggested by Whitten.[5] The hydrolysis of **7** or **8** gives diethylamine and acetaldehyde. Methyl isothiocyanate is probably produced from $\mathbf{1a}^{-\bullet}$, because the direct photolysis of **1a** does not give methyl isothiocyanate. Finally, diethylamine reacts with methyl isothiocyanate smoothly in the dark.



Scheme 2.

In the presence of DMN, the photoinduced electron transfer from the excited singlet state of DMN to **1a** occurs to give $\mathbf{1a}^{-\bullet}$ and $\mathrm{DMN}^{+\bullet}$. The former affords methyl isothiocyanate, which reacts with **2j** (Scheme 3). In this stage, the fate of $\mathrm{DMN}^{+\bullet}$ is not clear, because a hole transfer from **2j** to $\mathrm{DMN}^{+\bullet}$ is probably unfavorable.

In conclusion, we have found that a novel photoinduced electron transfer reaction of hypervalent sulfur compounds **1** with trialkylamines such as **2a–e** occurs to give dialkylaminated products **3** of alkyl isothiocyanates. From these results, we have clarified that **1** have both electron donating and electron accepting properties depending on the conditions. We believe that this is a rare example about the trapping of dialkylamines in the photoinduced electron transfer reaction of trialkylamines in the presence of an electron acceptor.



Scheme 3.

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