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Generation of Ketenes by Photolysis of Naphtho[1,8-*de*]-1,3-dichalcogeninylidene 1-Oxides

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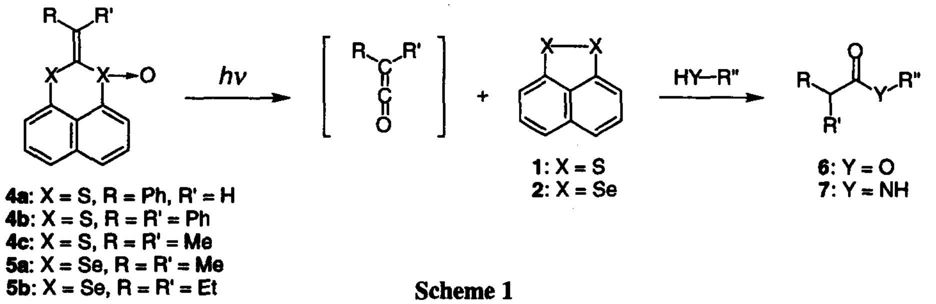
Abstract: The photolysis of naphtho[1,8-*de*]-1,3-dichalcogeninylidene 1-oxide derivatives (**4** and **5**) at >290 nm generates ketenes together with naphtho[1,8-*cd*]-1,2-dichalcogenole, which were confirmed by the trapping experiments and the direct observation using IR spectroscopy. The generation of ketenes from the selenium compounds **5** is more effective than that from the sulfur analogs **4**.

Keywords: Ketenes; Photochemistry; Selenium and compounds; Sulfur compounds

Ketenes are important reactive species, which occur as transients in numerous thermal and photochemical reactions.[1] Recently, ketenes generated by photolysis of α-diazocarbonyl compounds via Wolf-rearrangement have attracted attention as a DNA cleavage reagent.[2] For the generation of simple ketenes such as dimethyl ketene, however, the precursors have so far been restricted to α-diazocarbonyl compounds.

Through-space interaction between the two chalcogen atoms in 1,8-dichalcogen-substituted naphthalenes activates chalcogen-carbon bonds towards oxidants or photoirradiation.[3,4] The photolysis of naphtho[1,8-*de*]-1,3-dithiin 1-oxides,[5a] 1-*N*-tosyl-sulfilimines[5b] and 1-bis(ethoxycarbonyl)methylides[5c] produces carbonyl compounds, *N*-tosylaldimines and olefins, respectively, together with naphtho[1,8-*cd*]-1,2-dithiole (**1**). Here we report the photo-induced generation of ketenes from naphtho[1,8-*de*]-1,3-dithiinylidene 1-oxides (**4**) and naphtho[1,8-*de*]-1,3-diseleninylidene 1-oxides (**5**) (Scheme 1).



Scheme 1

Compounds **4** were prepared by the transformation of **1** to naphtho[1,8-*de*]-1,3-dithiin 1-oxide[5c,6] followed by the addition of carbonyl compounds to the carbanion and subsequent dehydration.[7] Compounds **5** were synthesized by the insertion of alkylidene carbenes into the Se-Se bond[8] of naphtho[1,8-*cd*]-1,2-diselenole (**2**) followed by the oxidation of the resulting naphtho[1,8-*de*]-1,3-diseleninylidenes (**3**).[7] The synthetic method for

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4 was not applicable for the preparation of **5**. Compounds **4** and **3** are thermally stable, whereas **5** are decomposed at ca. 60 °C (vide infra).

When a solution of **4** in deoxygenated 5% (v/v) MeOH-benzene at room temperature was irradiated at >290 nm with a 500 W high-pressure mercury lamp (method A), the corresponding methyl ester **6** and naphtho[1,8-*cd*]-1,2-dithiole (**1**) were obtained in good yields after purification with silica gel column chromatography. The representative results are summarized in Table 1. The compound **1** is recyclable as the synthetic building block of the substrates. The phenyl-substituted **4a** is reactive more than the diphenyl-substituted **4b**. The formation of **6** and **1** by the photolysis of **4** in the presence of MeOH strongly suggests the generation of ketene.

In order to compare the reactivity of the sulfur compounds **4** with that of the selenium compounds **5**, the reactions of **4** and **5** with 2 equiv of amines in deoxygenated benzene-$CHCl_3$ (4:1) at room temperature were carried out under irradiation at >290 nm with a 500 W high-pressure mercury lamp (method B) as shown in Table 1. The photoirradiation of **4a** in the presence of benzylamine gave the corresponding amide **7** (81%) and **1** (70%). On the other hand, the reaction of the dimethyl-substituted **4c** gave **7** (18%) and **1** (21%), where 3,3-dimethyl-naphtho[1,8-*de*]-1,3-dithiinylidene was obtained in 60% yield. Thus, the generation of ketenes strongly depends on the substituents of **4**. In marked contrast to **4c**, the photoirradiation of the dimethyl-substituted **5a** as a selenium analog of **4c** with benzylamine afforded **7** and naphtho[1,8-*cd*]-1,2-diselenole (**2**) in 73% and 60% yields, respectively. The rate for consumption of **5a** was faster than **4c** as monitored by ^1H NMR. There was no formation of 3,3-dimethyl-naphtho[1,8-*de*]-1,3-diseleninylidene (**3a**) during the course of reaction. The photolysis of the diethyl-substituted **5b** also gave **7** and **2** in good yields. These results show that the generation of ketenes from the selenium compounds **5** is more effective than that from the sulfur analogs **4**.

Table 1. Photolysis of **4** and **5** in the presence of trapping reagents[a]

Entry	Substrate	Trapping reagent	Method[b]	Time (h)	Isolated yields of products (%) 6	7	1	2
1	**4a**	MeOH	A	18	72		95	
2	**4b**	MeOH	A	58	42		52	
3	**4a**	$PhCH_2NH_2$	B	18		81	70	
4	**4c**	$PhCH_2NH_2$	B	18		18	21	
5	**5a**	$PhCH_2NH_2$	B	3		73		60
6	**5a**	$CH_3(CH_2)_{11}NH_2$	B	3		71		75
7	**5b**	$PhCH_2NH_2$	B	3		71		72

[a] Irradiation at >290 nm with 500 W high-pressure Hg lamp. [b] Method A: [4] = 4 mM in (v/v) 5% MeOH-benzene at room temperature; Method B: [substrate] = 54 mM and 2 equiv of amines in benzene-$CHCl_3$ (4:1) at room temperature.

In the present system, a through-space interaction between the two chalcogen atoms would play an important role in the generation of ketenes, because the framework having two chalcogen atoms in close proximity of naphthalene is essential for the reaction. The crystallographic analysis of **3a** as a precursor of **5a** reveals the Se···Se contact distance of 3.216(1) Å which is significantly shorter than twice the van der Waals radius of selenium (4.00 Å) (Figure 1).[9] The Se···Se contact distance of **5a** seems to be shorter than that of **3a**, because it has been found that the contact distance of sulfur atoms of naphtho[1,8-*bc*]-1,5-dithiocin 1-oxide is 0.23 Å shorter than that of the corresponding sulfide.[10] The mechanism may be explained by the initial photoexcitation of **4** and **5** to form the transient cyclic sulfenic esters **8** and selenenic esters **9**, respectively, probably due to the intramolecular migration of the sulfinyl and seleninyl oxygen atoms to the adjacent bridged-carbon atoms[11] via a chalcogen-chalcogen through-space interaction.[5] The photolysis of **8** and **9** would produce ketenes together with **1** and **2**, respectively.[5]

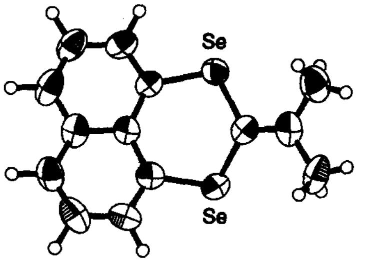
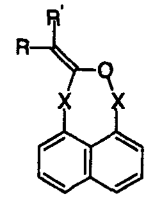


Figure 1. Crystal structure of **3a** (50% probability).



8: X = S
9: X = Se

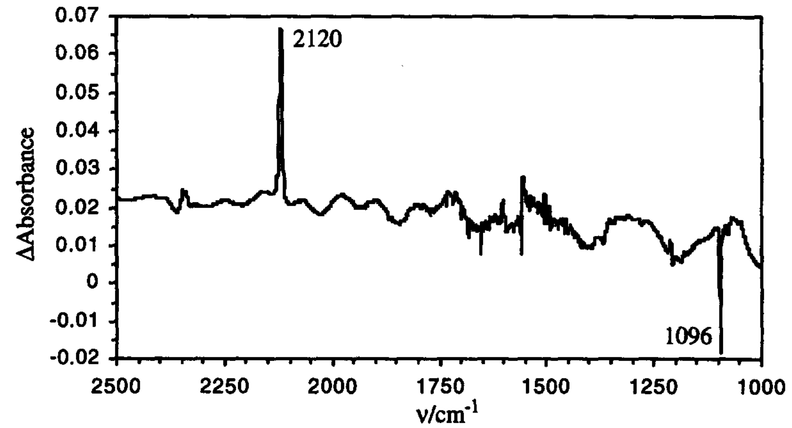


Figure 2. Difference of IR spectra of argon matrix-isolated **4a** at 11 K before and after irradiation at >290 nm for 2 h.

The generation of ketene was directly observed by the photolysis (>290 nm, 500 W high-pressure mercury lamp) of an argon matrix-isolated **4a** at 11 K, which was monitored by IR spectroscopy. The difference of IR spectra before and after irradiation for 2 h is shown in Figure 2. This result indicates a new characteristic band at 2120 cm^{-1} due to the C=C=O stretching band of phenyl ketene.[1,12] The intensity of phenyl ketene increases with increasing irradiation time, while the intensity of the S-O stretching band at 1096 cm^{-1} of **4a** decreases.[13]

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13. The selenium compound **5a** was thermally decomposed during the sublimation of **5a** at ca. 60 °C for the preparation of an argon matrix sample. However, products from the thermally decomposed **5a** were trapped in an argon matrix at 11 K and showed a new band at 2138 cm^{-1} due to the C=C=O stretching band of dimethyl ketene.[14]
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