CHEMISTRY LETTERS, pp. 1007-1010, 1994.

The Simple Preparation of Aldehydes and Ketones by the Photo-Oxygen Rearrangement of Naphtho[1,8-*de*]dithiin Monooxides

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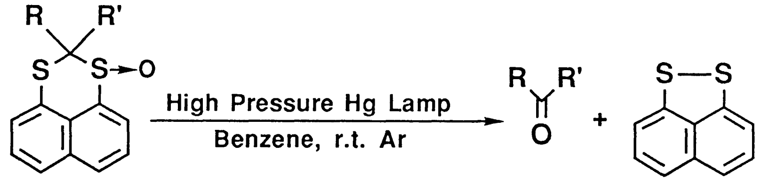
Naphthalene-1,8-dithiol reacted with aldehydes to give dithioacetals which were oxidized to 2-substituted naphtho[1,8-*de*]1,3-dithiin-1-oxides (**4**). 2, 2-Disubstituted naphtho[1,8-*de*]1,3-dithiin-1-oxides (**5**) were obtained on treatment of **4** with NaH/ electrophiles. Photolysis of **4** and **5** undergoes intramolecular oxygen rearrangement to generate aldehydes and ketones quantitatively together with naphthalene-1,8-dithiole.

In general, 1,3-dithianes and related derivatives have been utilized as carbonyl synthones1) in organic synthesis since they readily provide aldehydes and ketones by desulfurization with many efficient methods such as metal-induced,2) oxidative,3) alkylative,4) photo-induced,5) and electrolytic6) decompositions or by hydrolysis of the corresponding monooxides with strong acids.7)

1,8-Dithia or -diselena naphthalene derivatives are presumably the candidates for generating various active species or creating new reactions via the formation of reactive dithia- or diselena dications.8) In fact, 1,8-dithia or -diselena naphtho[1,8-*bc*]dithiocins undergo unusual Pummerer and thio-Claisen rearrangement reactions via the formation of dications.9) Furthermore, quinodimethane is generated from photolysis of 8,13-dihydrobenzo[*g*]naphtho[1,8-*bc*][1,5]diselenonin.10) As a further extension of these studies, we prepared naphtho[1,8-*de*]dithiins and found that photolysis of the corresponding monooxides became a convenient procedure to yield the carbonyl compounds. This paper reports the results on the photo-oxygen rearrangement reaction of naphtho[1,8-*de*]dithiin monooxides to the aldehydes and ketones.

1,8-Naphthalene dithiol (**1**) was treated with aldehydes in the presence of $SiCl_4$ in CH_2Cl_2 affording the corresponding 2-substituted naphtho[1,8-*de*]1,3-dithiins (**2**) in high yields.11) However, 2, 2-disubstituted naphtho[1,8-*de*]1,3-dithiins (**3**) were obtained in poor yields on analogous treatment with ketones and **1** and hence dithioketals **3** were prepared from the reaction of 2-lithiated **2** with several electrophiles. 2-Substituted naphtho[1,8-*de*]1,3-dithiin-1-oxides (**4**) and 2, 2-disubstituted naphtho[1,8-*de*]1,3-dithiin-1-oxides (**5**) were obtained in high yields with high diastereo-selectivities (for instance, diastereomeric ratios of **4a**, **4b**, and **4d** determined by ^{1}H NMR spectroscopy were found to be 5:1, 7:1, and 3:1 respectively) by oxidation using *m*-chloroperbenzoic acid (*m*CPBA) in CH_2Cl_2 at -20 °C.11) Furthermore, compounds **4** were also converted to dithioketal monooxides **5** by the reaction with NaH in THF at 50 °C and then with several electrophiles in moderate yields.11) Although compounds **2** and **3** were thermally and photochemically stable molecules, monooxides **4** and **5** were found to decompose to the corresponding aldehydes and ketones quantitatively with complete recovery of naphthalene-1, 8-dithiole (**8**) on exposure to high pressure mercury lamp (400 W) in benzene for 20 h (Scheme 1). After evaporation of benzene and work-up, the residue was chromatographed to give **7** and **8** quite readily (Table 1). As shown in Table 1, the results reveal that the reactions are clean and aldehydes or ketones were obtained quantitatively with the recovered naphthalene-1, 8-dithiole (**8**). Other five- and six-membered 1,3-dithia derivatives **9** and **10** were unreactive under the present photolysis conditions. Although 1-naphthyldithioacetal monooxide (**11**) underwent photodecomposition under identical conditions, the products obtained were a mixture of intractable compounds which were unable to separate by a simple procedure. Therefore, the mechanism for the decomposition of **4** and **5** can be explained by the initial photo-excitation of the sulfoxides to form the reactive intermediates **6** probably by the intramolecular migration of the sulfinyl oxygen atom to the 2-carbon atom *via* the S-S through space interaction. The photochemical oxygen migration of sulfoxides has been reported in the literature.[12] Finally, the intermediate sulfenic esters **6** should be converted to the corresponding aldehydes or ketones and naphthalene-1, 8-dithiole (**8**).



4: R=Alkyl, Aryl; R'=H
5: R, R'=Alkyl, Aryl

7 8

Scheme 1.

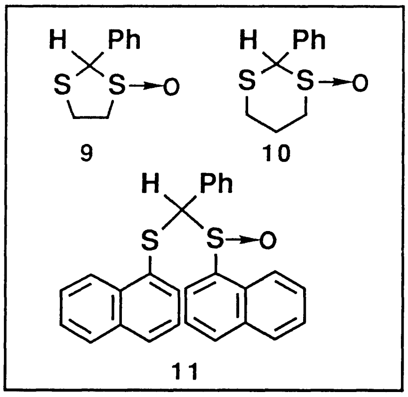
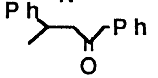

9 10 11

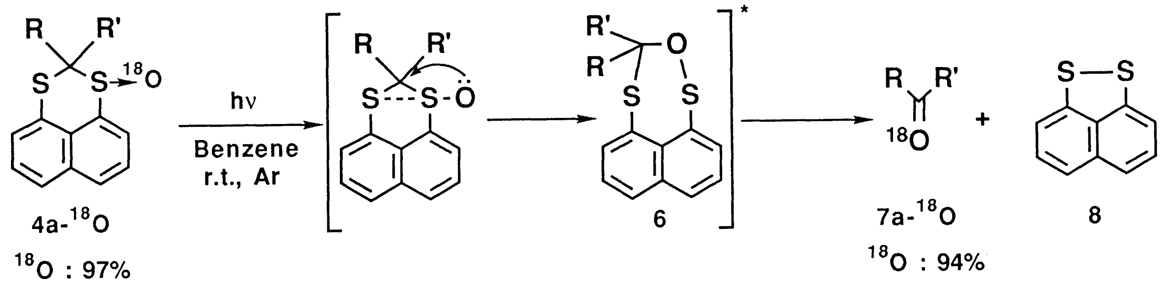
Table 1. Photolysis of Dithioacetal Monooxides **4** and Dithioketal Monooxides **5** in Benzene[a)]

	R	R'	Yield of **7**/%[b)]	Yield of **8**/%[b)]
4a	Ph	H	>99	>99
4b	$CH_3(CH_2)_5$	H	>99	>99
4c	PhCH=CH	H	>99 (97)[c)]	>99 (98)[c)]
4d		H	>99	>99
5a	Ph	D	>99	>99
5b	Ph	CH_3	>99 (93)[c)]	>99 (100)[c)]
5c	Ph	CH_3CH_2	>99 (95)[c)]	>99 (99)[c)]
5d	Ph		>99 (96)[c)]	>99 (98)[c)]
5e	Ph		>99 (98)[c)]	>99 (100)[c)]
5f	Ph	PhCH(OH)-	- (82)[c)]	- (91)[c)]
5g	Ph	$PhCH(OCH_3)$-	>99 (97)[c)]	>99 (98)[c)]

a) 400 W high pressure Hg lamp, λ> 300 nm, Substrates (0.1 mmol), Benzene (5 ml). b) Yields were determined by gas chromatography and ^1H-NMR spectroscopy. c) Isolated yields.

In order to understand the mechanism for the oxygen migration ^{18}O labelled compound **4a**-^{18}O (^{18}O content=97 %) was prepared and subjected to photolysis under irradiation with a high pressure Hg lamp. The contents of ^{18}O were determined with mass spectrometric measurement. The sulfinyl ^{18}O labelled in **4a** was found to migrate completely to the oxygen atom of benzaldehyde (^{18}O content=94 %) as shown in Scheme 2.

Furthermore, 2-deuterated 2-phenyl-naphtho[1,8-*de*]1,3-dithiin-1-oxide (**5a**) was also photolyzed under identical conditions as described above to result in the formation of benzaldehyde-1D (D>99%).$^{13)}$ Thus, this photolysis of the compounds **4a** and **5a** are a convenient process to prepare the ^{18}O and D labelled aldehydes.



Scheme 2.

Recently, Foote et al. and Clenann et al. have reported the photooxidation of 1,5-dithiacyclooctane with oxygen in the presence of a sensitizer, in which they have described that the transannular S-S interaction determines the product formation.$^{14)}$ Furthermore photolysis of simple dithianes or dithiolanes in the presence of dyes as sensitizers has also been reported to give aldehydes or ketones in high yields.$^{15)}$ The "environmentally benign" nature of the procedure has been stressed to be advantageous in synthetic organic chemistry.

The advantage of our present procedure is a promised method to prepare aldehydes and ketones in high yields without use of either unpleasant-smelling alkyldithiols or toxic heavy metals or strong acids for deprotection. Furthermore, the starting material naphthalene-1, 8-dithiole (**8**) can be recovered completely and recycled after the reactions.

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11) The compounds **2**, **3**, **4**, and **5** were prepared and their structures were determined by ^{1}H- , ^{13}C-NMR, and mass spectrometries. They gave satisfied elemental analysis.

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(Received February 28, 1994)