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PHOTOCHEMICAL TRANSFORMATION OF A DITHIOACETAL S-OXIDE INTO THE CORRESPONDING ALDEHYDE

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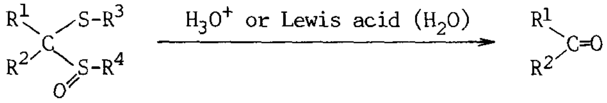
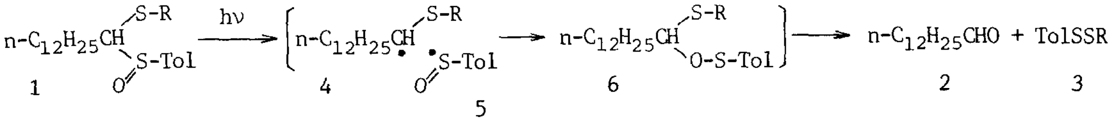
Summary: Irradiation of an aldehyde dithioacetal S-oxide gives the corresponding aldehyde. The mechanism of this photochemical transformation is discussed and its application to organic synthesis is also described.

Dithioacetal S-oxides are very useful reagents for making a variety of organic compounds, where the acid-catalyzed conversion of dithioacetal S-oxide functionality to the corresponding carbonyl group is one of the most important steps.[1]



During the course of our investigation to develop further utility of the dithioacetal S-oxide functionality in organic synthesis including an asymmetric synthesis, we have found that ultraviolet irradiation makes it possible to produce an aldehyde from the corresponding dithioacetal S-oxide having p-tolyl group on its sulfinyl sulfur under neutral or basic conditions. This finding enables the use of this functionality for preparing of an acid-sensitive aldehyde.



a: R = CH_3 b: R = Tol [Tol = p-tolyl]

Irradiation of a tridecanal dithioacetal S-oxide (1a) with a low-pressure Hg lamp (Pyrex filter) under bubbling with N_2 afforded tridecanal (2). The results are summarized in Table 1, which shows that the photochemical reaction of 1a to give 2 takes place in hexane, dioxane, dioxane-water, or methanol. Bubbling with O_2 significantly decreased the yields of 1a and 2, suggesting that this reaction might involve an radical intermediate. Analogous tendencies were also observed in the photolysis reaction of a di-p-tolyl dithioacetal S-oxide (1b). Since 1 absorbs the light of longer than 290 nm wavelength (Fig. 1), a high-pressure Hg lamp through a Pyrex filter can be employed for the photolysis of 1 as shown in Table 2. Under these conditions, benzophenone accelerates the reaction, whereas an electron-transfer sensitizer, 1-(dimeth-

Table 1. Photolysis of 1 with 254 nm Light[a]

No.	substrate	solvent	bubbling gas	additive (equiv)	irradiation time/min	yield/%[b] 1	yield/%[b] 2
1	1a	hexane	N_2	--	30	0	22
2	1a	hexane	N_2	--	10	52	33(68)
3	1a	dioxane	N_2	--	30	13	56(64)
4	1a	dioxane-H_2O(9:1)	N_2	--	30	21	58(73)
5	1a	dioxane-H_2O(9:1)	N_2	$NaHCO_3$(3)	30	17	61(73)
6	1a	dioxane-H_2O(9:1)	O_2	--	30	0	2
7	1a	methanol	N_2	$NaHCO_3$(3)	30	10	58(64)
8	1b	hexane	N_2	--	60	7	44(47)
9	1b	dioxane	N_2	--	60	12	48(55)
10	1b	dioxane-H_2O(9:1)	N_2	--	60	12	62(70)
11	1b	dioxane-H_2O(9:1)	N_2	$NaHCO_3$(3)	60	13	62(71)
12	1b	dioxane-H_2O(9:1)	O_2	--	60	0	43

a: 1 (about 1 mmol) was irradiated with a low-pressure Hg lamp (10 W) through a Vycor filter under cooling with tap water. b: ( ) = the yield based on the unrecovered 1.

ylamino)naphthalene, was less effective. These facts are in sharp contrast with the photochemical reaction of the corresponding S,S-dioxide to afford 2, where benzophenone does not serve as a sensitizer, but 1-(dimethylamino)-naphthalene does.[2]

In order to provide some insights into the mechanism of the reaction, we irradiated the ^{18}O-labeled derivative (7) of 1b. When 7 (87% content of ^{18}O)[3] was irradiated in anhydrous THF with a low-pressure Hg lamp and the reaction mixture was subjected to the usual workup and column chromatography, ^{18}O was not detected in the isolated 2. This is probably due to the fast exchange of ^{18}O of 2 during the workup or the chromatographic separation. Hence, L-Selectride was directly added to the irradiated mixture to reduce the formed 2. The isolated 1-tridecanol exhibited the fragment of $CH_2O^{18}H$ in its mass

Table 2. Photolysis of 1 with >290 nm light[a]

No.	1	Additive	1/%	2/%
1	1a	--	0	48
2	1a	DAN[b](1 mol-equiv)[b]	53	29
3	1a	PhCOPh (1 mol-equiv)	0	40
4	1b	--	28	20
5	1b	DAN[b](1 mol-equiv)	68	19
6	1b	PhCOPh (1 mol-equiv)	0	37

a: irradiated with a 100-W high-pressure Hg lamp through a Pyrex filter in dioxane-H_2O (9:1) under bubbling with N_2 for 8 h. b: DAN = 1-(dimethylamino)naphthalene.

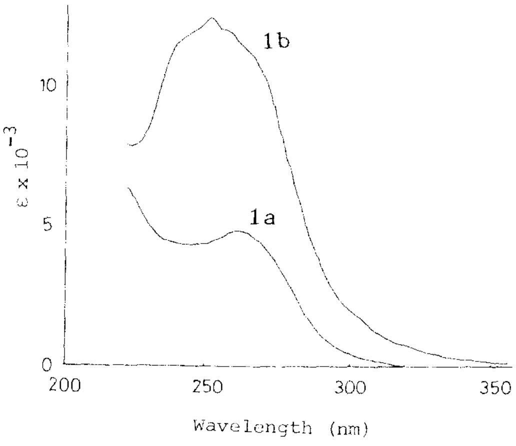
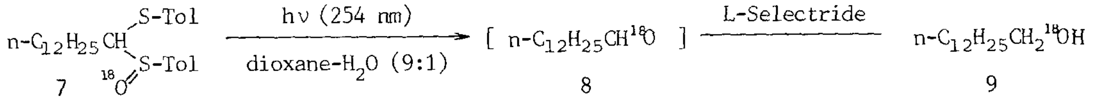


Figure 1. UV Spectrum of 1 in Dioxane

spectrum. From the intensity of this fragment, the ^{18}O content of 1-tridecanol was calculated to be 73%. Thus the origin of the oxygen of 2 was indicated to be the oxygen of the sulfinyl group of 1.



$$\text{n-C}_{12}\text{H}_{25}\text{CH}\langle{}^{\text{S-Tol}}_{\text{S(}={}^{18}\text{O)-Tol}} \xrightarrow[\text{dioxane-H}_2\text{O (9:1)}]{h\nu\ (254\ \text{nm})} [\ \text{n-C}_{12}\text{H}_{25}\text{CH}^{18}\text{O}\ ] \xrightarrow{\text{L-Selectride}} \text{n-C}_{12}\text{H}_{25}\text{CH}_2{}^{18}\text{OH}$$

7 8 9

This finding as well as the effect of bubbling with O_2 and the sensitization experiment supports the reaction path depicted in Scheme 1 for the photochemical conversion of 1 to 2: The reaction is initiated from the triplet excited state of 1 to afford two radical species (4 and 5). The recombination of 4 with the O-site of 5 forms a thioacetal (6), which thermally decomposes to give 2 along with a disulfide (3).

The intermediary existence of the thioacetal 5 may be suggested by the following observation: After a $CDCl_3$ solution of 1a was externally irradiated in a NMR tube with a high-pressure Hg lamp under cooling with ice, the NMR spectrum was immediately measured to show a weak signal in the region of formyl proton. However, after being allowed to stand at 37 °C for 4 min, an intense signal of the formyl proton of 2 appeared (Figure 2).

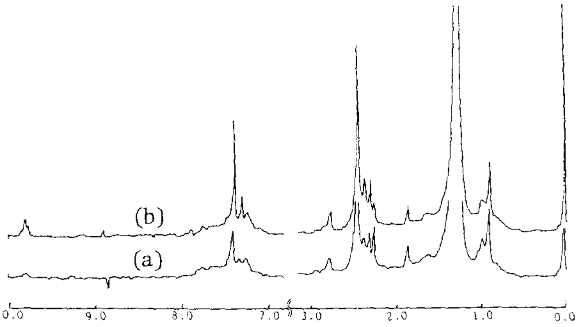
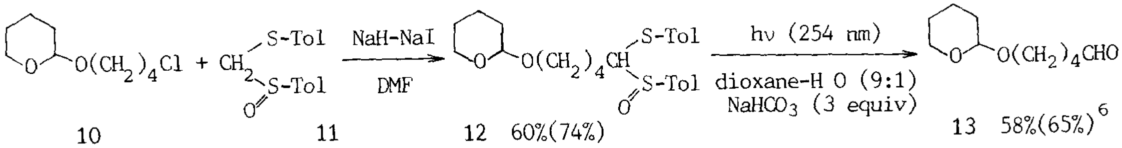


Figure 2. ^{1}H NMR Spectrum of the Irradiated 1a

(a) Immediately after irradiation at 0 °C.
(b) After being allowed to stand at 37 °C for 4 min.

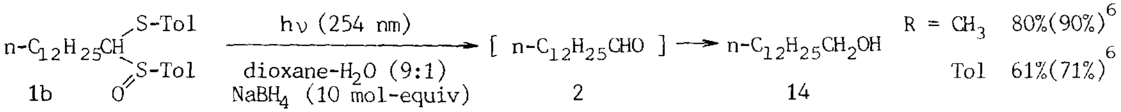
Since methylthio group more strongly stabilizes the radical of its α-position than phenyl group,[5] it may be reasonably assumed that the life time of the intermediary radical 4b is shorter than that of 4a. This seems to reflect on the effect of bubbling with O_2 which retards the formation of 2 from 1b to a larger extent than from 1a.

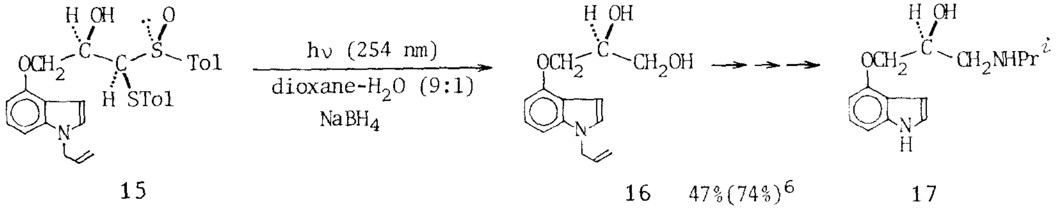
The present reaction was not interrupted by $NaHCO_3$ which enables the present photolysis under basic conditions. This appears well suited for the preparation of an aldehyde having an acid-sensitive group, as exemplified by the synthesis of 5-(2-tetrahydropyranyloxy)pentanal (13) using formaldehyde di-p-tolyl dithioacetal S-oxide (11).



10 11 12 60%(74%) 13 58%(65%)[6]

Further we have found that the photolysis of 1 in the presence of $NaBH_4$ gave 1-tridecanol (14) which might be produced by the reduction of the primarily formed tridecanal. The photolysis in the copresence of $NaBH_4$ is suitably employed when the desired product is the corresponding alcohol: A dithioacetal S-oxide (15) was irradiated in dioxane-water (9:1), but we could not isolate the corresponding aldehyde. This might be attributable to its instability under acidic, neutral, and basic conditions. Hence, 15 was irradiated in the presence of $NaBH_4$ (10 mol-equiv) with a low-pressure Hg lamp to directly yield the corresponding alcohol (16), which is a synthetic precursor of a β-blocker drug, (S)-pindolol (17).





Thus, the photolysis of a dithioacetal S-oxide has been shown to provide a method for producing the corresponding aldehyde under neutral or basic conditions. The scope of the present photochemical reaction and its application to an asymmetric synthesis using optically active formaldehyde di-p-tolyl dithioacetal S-oxide is one of our on-going subjects.

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References and Footnotes

1. K. Ogura and G. Tsuchihashi, Tetrahedron Lett., 3151 (1971) and 2681 (1972); J. E. Richman, J. L. Herrmann, and R. H. Schlessinger, ibid., 3267 and 3275 (1973); J. L. Herrmann, J. E. Richman, and R. H. Schlessinger, ibid., 3271 (1973); J. L. Herrmann, J. E. Richman, P. J. Wepplo, and R. H. Schlessinger, ibid., 4707 (1973); J. L. Herrmann, G. Kieczykowski, R. F. Romanet, P. J. Wepplo, and R. H. Schlessinger, ibid., 4711 (1973); J. L. Herrmann, G. R. Kieczykowski, R. F. Romanet, and R. H. Schlessinger, ibid., 4715 (1973); G. Schill and P. R. Jones, Synthesis, 117 (1974); L. Colombo, C. Gennari, and C. Scolastico, J. Chem. Soc., Perkin Trans. I, 1278 (1981); L. Colombo, C. Gennari, G. Resnati, and C. Scolastico, J. Chem. Soc., Perkin Trans. I, 1284 (1981); K. Ogura, M. Fujita, T. Inaba, K. Takahashi, and H. Iida, Tetrahedron Lett., 24, 503 (1983); K. Ogura, M. Yamashita, M. Suzuki, S. Furukawa, and G. Tsuchihashi, Bull. Chem. Soc. Jpn., 57, 1637 (1984).
2. K. Ogura, K. Ohtsuki, K. Takahashi, and H. Iida, an unpublished result. For the photochemical conversion of a dithioacetal S,S-dioxide to the corresponding aldehyde, K. Ogura, K. Ohtsuki, M. Nakamura, K. Takahashi, and H. Iida, Tetrahedron Lett., 26, 2455 (1985).
3. This compound was obtained by alkylation of ^{18}O-labeld formaldehyde di-p-tolyl dithioacetal S-oxide which was prepared by oxidation of formaldeyde di-p-tolyl dithioacetal with bromine and $H_2{}^{18}O$ in dichloromethane.[4]
4. J. Drabowicz, W. Midura, and M. Mikołajczyk, Synthesis, 39 (1979).
5. A. Ohno and Y. Ohnishi, Tetrahedron Lett., 4405 (1969); B. K. Bandlish, A. W. Garner, M. L. Hodges, and J. W. Timberlake, J. Am. Chem. Soc., 97, 5856 (1975).
6. ( ) = the yield based on the unrecovered starting material.

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