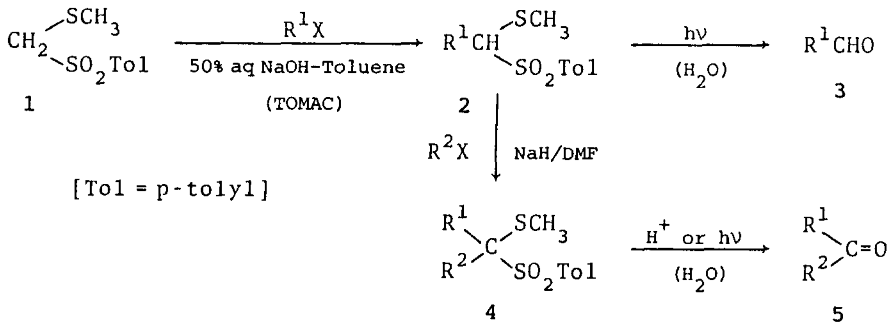
Tetrahedron Letters,Vol.26,No.20,pp 2455-2458,1985 0040-4039/85 $3.00 + .00
Printed in Great Britain

ALDEHYDE AND KETONE SYNTHESES USING METHYLTHIOMETHYL p-TOLYL SULFONE

Katsuyuki Ogura*, Kazuo Ohtsuki, Masami Nakamura, Nobuhiro Yahata, Kazumasa Takahashi, and Hirotada Iida
Department of Synthetic Chemistry, Faculty of Engineering,
Chiba University, Yayoicho 1-33, Chiba 260, Japan

Abstract: Methylthiomethyl p-tolyl sulfone (1) was conveniently alkylated to give mono- and dialkylated products (2 and 4). Reaction conditions for the trasformation of 2 and 4 into aldehydes (3) and ketones (5), respectively, were exploited.

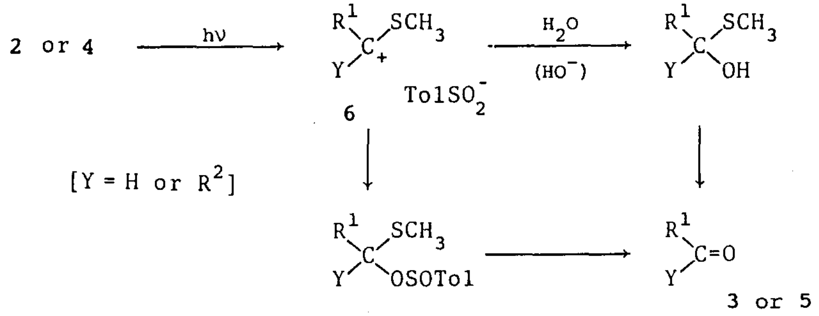
Our previous papers showed that methylthiomethyl p-tolyl sulfone (1)[1] could be utilized in the preparation of carboxylic esters from alkyl halides,[2] S-methyl-α-ketocarbothioates[2] and carbaldehydes[3] from carboxylic esters, cyclic ketones from 1,n-dihaloalkanes,[2] and α-alkoxy-α-arylacetic esters from aromatic carbaldehydes.[2] In this letter, we wish to report that 1 also is useful for preparing aldehydes and ketones. The accompanying scheme summarizes the present pathways: Alkylation of 1 to give the corresponding mono- and dialkylated products (2 and 4) and the subsequent hydrolysis of the dithioacetal S,S-dioxide group of 2 and 4 are comprised.



Compared with the conventional methods using formaldehyde dithioacetals and their S-oxides,[4,5] the present one has two distinct features: (i) the alkylation of 1 utilizes an inexpensive and easily-handled base and (ii) the hydrolysis of 2 and 4 can be conducted under basic conditions which make it possible to prepare aldehydes and ketones with acid-sensitive fuctional group(s).

As already reported, 1 can generate a carbanion at its methylene carbon so easily that monoalkylation of 1 with an alkyl halide proceeds under the so-called "two-phase reaction" using 50% aq. NaOH as a base and trioctylmethylammonium chloride (TOMAC) as a phase-transfer catlyst.[2] Further, we have found that NaH can cleanly abstract the proton of 2 at room temperature in DMF to produce the corresponding carbanion, which gave the dialkylated product (4) in the reaction with the coexisting alkyl halide. The combination of this fact with the acid-assisted hydrolysis of ketone dithioacetal S,S-dioxide groups[5,6] provides a convenient synthetic route leading to symmetrical and unsymmetrical ketones (5). Table 1 summarized these results. For the preparation of symmetrical ketones, direct dialkylation of 1 with an alkyl halide and NaH in DMF is recommended.

To our surprise, the monoalkylated product (2) resisted the above-mentioned hydrolysis. Thus, 2 (R^1= n-$C_{12}H_{25}$) was quantitatively recovered even after being heated in conc HCl-methanol (1:10) under a reflux for 24 h. Hence, our investigation was initiated to exploit a new type of reaction for the conversion of 2 and 4 into 3 and 5, respectively: When heterolytic cleavage of the C-SO_2 bond of 2 and 4 is photochemically forced to take place, capture of the resulting carbenium ion (6) with water or hydroxide anion and the subsequent removal of methanethiol moiety produce 3 and 5.



When a solution of 2 (R^1= n-$C_{12}H_{25}$) in dioxane-water (19:1) was irradiated with a low-pressure Hg arc lamp (10 W) through a Vycor filter, a smooth reaction took place in the presence or absence of a base ($NaHCO_3$ or NaOH) to give tridecanal (3: R^1= n-$C_{12}H_{25}$). Under the same conditions, 1-methylsulfonyl-1-(methylthio)tridecane remained unchanged, indicating that the photochemical transformation of 2 is initiated by the light absorption of the p-tolyl group. Since the photolytic formation of 3 (R^1= n-$C_{12}H_{25}$) was not influenced by oxygen-bubbling and the employment of ethanol as a solvent

Table 1. Ketone Synthesis Using 1

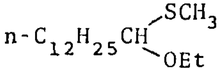
Starting Material	Alkyl Halide (equiv)	Alkylation[a] Temp(°C)/Time(h)	Hydrolysis[b] Temp/Time(h)	Overall Yield
2; R = $PhCH_2$	CH_3I (3.1)	[A] rt/19	[D] reflux/2	96%
2; R = $PhCH_2$	n-$C_6H_{13}Br$ (2.0)	[A] rt/48 → 50/3	[D] reflux/3	92%
2; R = CH_3	$PhCH_2Br$ (1.5)	[A] rt/48 → 60/3	[E] reflux/3	85%
2; R = n-$C_{12}H_{25}$	CH_3I (2.4)	[A] rt/42	[D] reflux/3	90%
1	$PhCH_2Br$ (2.3)	[B] rt/48 → 60/3	[E] reflux/3	74%
1	n-$C_{12}H_{25}Br$ (2.6)	[B] rt/48 → 50/3	[E] reflux/3	93%
1	$Br(CH_2)_5Br$ (1.0)	[C] 60/144	[D] reflux/3	91%[c]
1	$Br(CH_2)_4Br$ (1.0)	[C] 60/96	[D] reflux/5	98%[c]
1	$Br(CH_2)_3Br$ (1.1)	[B] -15/6 → rt/18	[F] 100 °C/20	83%

[a] [A]: with NaH (1.3 equiv)/DMF, [B]: with NaH (2.5 equiv)/DMF, [C]: with TOMAC (0.02 equiv)/toluene-50% aq NaOH. [b] [D]: with conc HCl/MeOH (0.3-1/10 v/v), [E]: with conc H_2SO_4/MeOH (0.5-1/10 v/v), [F]: with conc HCl/dioxane (1/10 v/v). [c] ref. 2.

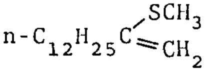
Table 2. Photo-induced Hydrolysis of 2 and 4[a]

R^1	R^2	Solvent	Base[b]	Atmosphere	3 or 5	2 or 4	( )[c]
2; n-$C_{12}H_{25}$	-	Dioxane	---	N_2	26%[d]	29%	(36%)
2; n-$C_{12}H_{25}$	-	Dioxane-H_2O (19:1)	---	N_2	67%	28%	(93%)
2; n-$C_{12}H_{25}$	-	Dioxane-H_2O (19:1)	$NaHCO_3$	N_2	61%	25%	(82%)
2; n-$C_{12}H_{25}$	-	Dioxane-H_2O (19:1)	$NaHCO_3$	O_2	63%	0%	
2; n-$C_{12}H_{25}$	-	EtOH-H_2O (19:1)	$NaHCO_3$	N_2	24%[e]	31%	
2; n-$C_{12}H_{25}$	-	Dioxane-H_2O (19:1)	NaOH	N_2	72%	18%	(89%)
2; 4-ClC_6H_4	-	Dioxane-H_2O (19:1)	$NaHCO_3$	N_2	20%	35%	(33%)
4; n-$C_{12}H_{25}$	CH_3	Dioxane-H_2O (19:1)	$NaHCO_3$	N_2	46%[f]	--[g]	
4; n-$C_{12}H_{25}$	CH_3	Dioxane-H_2O (19:1)	NaOH	N_2	58%[h]	--[g]	
4; -$(CH_2)_5$-		Dioxane-H_2O (19:1)	$NaHCO_3$	N_2	67%[i]	--[g]	

[a] a solution of 2 or 4 (~500 mg/200 ml) was irradiated with a low-pressure Hg arc lamp (10 W) through a Vycor filter under being externally cooled with water. [b] three equiv to 2 or 4. [c] the yield of 3 based on the unrecovered 2. [d] the trioxane derivative of tridecanal (33%) was also obtained. [e] 7 (38%) was formed. [f] 2-methylthio-1-tetradecene (8) was given in 29% yield. [g] not determined. [h] 8 (28%) was produced. [i] trapped as its 2,4-dinitrophenylhydrazone.


$n\text{-}C_{12}H_{25}CH(SCH_3)(OEt)$

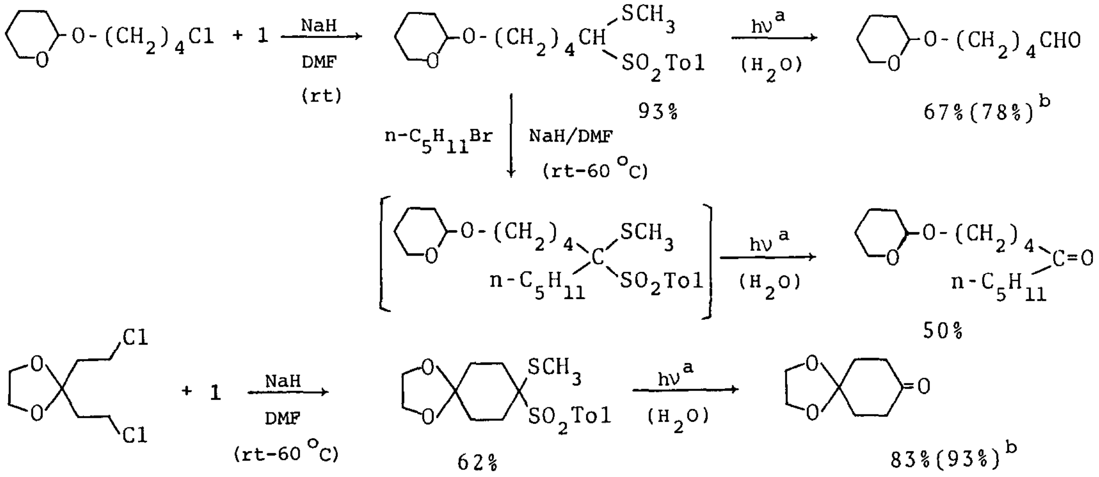
7


$n\text{-}C_{12}H_{25}C(SCH_3){=}CH_2$

8

produced 1-ethoxy-1-(methylthio)tridecane (7), the photochemical transformation of 2 into 4 might involve the cation (6) produced by the heterolytic fission of the C-SO_2 bond. At the present time, we cannot exclude the possibility that 3 is partially formed via 1-methylthio-1-(p-toluenesulfinato)alkane given by the recombination of 6 and p-toluenesulfinate anion. In the similar manner, ketones (5) were afforded as shown in Table 2.

Thus we have developed a new method for the hydrolysis of a dithioacetal S,S-dioxide group to afford the corresponding carbonyl group. Since this hydrolysis can be conducted in the presence of a base, the present routes from 1 to 3 and 5 are suitably applicable to the preparation of aldehydes and ketones which are susceptible to an acid. A few examples are shown in the following.



[a] with a low-pressure Hg arc lamp (Vycor filter) in dioxane-H_2O (19:1) containing 3 equiv of $NaHCO_3$. [b] based on the unrecovered starting material.

Now we are investigating the scopes and limitation of the aldehyde and ketone syntheses using 1, and a detailed mechanistic study on the photo-induced hydrolysis of dithioacetal S,S-dioxide groups is our on-going subject.

References and Footnotes

1) This reagent (1) can be conveniently prepared from dimethyl sulfoxide: K. Ogura, N. Yahata, J. Watanabe, K. Takahashi, and H. Iida, Bull. Chem. Soc. Jpn., **56**, 3543 (1983). Now 1 is commercially available from Nissan Chemical Industries Ltd.
2) K. Ogura, N. Yahata, K. Hashizume, K. Tsuyama, K. Takahashi, and H. Iida, Chem. Lett., **1983**, 767.
3) K. Ogura, N. Yahata, K. Takahashi, and H. Iida, Tetrahedron Lett., **24**, 5761 (1983).
4) Formaldehyde diethyl dithioacetal: J. F. Arens, M. Fröling, and A. Fröling, Rec. Trav. Chim. Pays-Bas, **78**, 663 (1959); A. Fröling and J. F. Arens, Rec. Trav. Chim. Pays-Bas, **81**, 1009 (1962). 1,3-Dithiane: D. Seebach, Synthesis, **1969**, 17. Formaldehyde dimethyl dithioacetal S-oxide: K. Ogura and G. Tsuchiahsi, Tetrahedron Lett., **1971**, 3151. Formaldehyde diethyl dithioacetal S-oxide: J. E. Richman, J. L. Herrmann, and R. H. Schlessinger, Tetrahedron Lett., **1973**, 3267.
5) K. Ogura, M. Suzuki, J. Watanabe, M. Yamashita, H. Iida, and G. Tsuchihashi, Chem. Lett., **1982**, 813.
6) Y. Murata, K. Inomata, H. Kinoshita, and H. Kotake, Bull. Chem. Soc. Jpn., **56**, 2539 (1983).

(Received in Japan 21 February 1985)