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A NOVEL SYNTHESIS OF HALF-PROTECTED 1,3-DICARBONYL COMPOUNDS

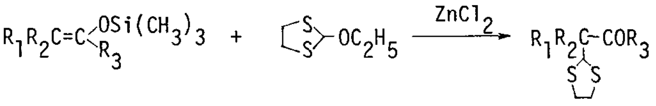
Kouhei Hatanaka,* Shigeo Tanimoto,* Toyonari Sugimoto and Masaya Okano

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611, Japan

Summary: It has been found that the reaction of enol silyl ethers with 2-ethoxy-1,3-dithiolane proceeds smoothly in the presence of zinc chloride catalyst to afford half-protected 1,3-dicarbonyl compounds in moderately good yields.

In 1959, it was shown that several β-chlorovinyl ketones are able to react with 1,2-ethanedithiol in the presence of potassium carbonate to give (1,3-dithiolan-2-yl)methyl ketones.[1] Recently, Taylor and his co-worker[2] described a process for the introduction of a base-stable protected formyl substituent to carbonyl compounds. This procedure involves the reaction of 2-chloro-1,3-dithiane with the morpholino enamines of the carbonyl compounds.

In the present communication, we show that enolizable aldehydes or ketones can be converted to the half-protected 1,3-dicarbonyl compounds 2 by reaction of their enol silyl ethers (1-alkenyl silyl ethers) 1 with 2-ethoxy-1,3-dithiolane in the presence of zinc chloride. The conversion can be effected most cleanly and efficiently using the zinc chloride catalyst, since the formation of 2,2'-[1,2-ethanediylbis(thio)]bis-1,3-dithiolane[3] as a by-product from 2-ethoxy-1,3-dithiolane is avoided in contrast to the use of aluminum chloride, titanium(IV) chloride or boron trifluoride etherate. The yields of the products[4] under various conditions are summarized in Table 1.



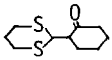
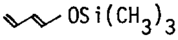
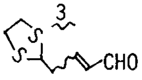
1

2

a R_1=H, R_2=C_2H_5, R_3=H
b R_1=H, R_2=$CH_3(CH_2)_5$, R_3=H
c R_1=R_2=CH_3, R_3=H
d R_1=H, R_2, R_3= $-(CH_2)_4-$
e R_1=H, R_2,R_3= $-(CH_2)_3-$
f R_1=R_2=H, R_3=C_6H_5
g R_1=H, R_2=CH_3, R_3=C_2H_5
h R_1=R_2=H, R_3=$C(CH_3)_3$
i R_1=H, R_2=C_2H_5, R_3=OC_2H_5
j R_1=H, R_2=$CH_3(CH_2)_2$, R_3=OC_2H_5

The following general experimental procedure is representative of this conversion. To a stirred, cooled (0°C) mixture of 2.4 mmol of the appropriate enol silyl ether and 0.30 g (2.0 mmol) of 2-ethoxy-1,3-dithiolane in 2 ml of acetonitrile or in 2 ml of dichloromethane (or without any solvent) is added during about 1–2 min 0.1 g (0.75 mmol) of zinc chloride. After addition is complete, the mixture is stirred at 0°C or room temperature (20–25°C) for such time till the complete consumption of the added 2-ethoxy-1,3-dithiolane which is ascertained by thin-layer chromatography. Then it is poured into 50 ml of cold brine, and extracted with several portions of ether. The combined extracts are dried ($MgSO_4$), filtered, and concentrated *in vacuo* to give a pale yellow colored residue. The product is isolated by column chromatography on silica gel with 5% ethyl acetate–hexane as the eluent. The results using 1 and 2-ethoxy-1,3-dithiolane were more satisfactory than Taylor's results[2] in view of the yield. Considering that both of the starting reagents are readily available, the present method provides one of the most convenient routes for the preparation of half-protected 1,3-dialdehydes and β-keto aldehydes.

Table 1. Reaction of Enol Silyl Ethers with 2-Ethoxy-1,3-dithiolane in the Presence of $ZnCl_2$

Enol silyl ether	Product	Reaction conditions(solvent/temperature,°C/time,hr) and yield of 2 (%)
1a	2a	CH_3CN/20-25/18(65), CH_2Cl_2/20-25/18(19), neat/20-25/3(35)
1b	2b	CH_3CN/20-25/48(70), CH_2Cl_2/0/3(73), neat/0/3(81)
1c	2c	CH_3CN/20-25/12(54), CH_2Cl_2/20-25/2(60), neat/20-25/3(42)
1d	2d	CH_3CN/20-25/6(94), CH_2Cl_2/20-25/1(77), neat/20-25/1(78)
1e	2e	CH_3CN/20-25/12(77), CH_2Cl_2/20-25/12(69), neat/20-25/12(75)
1f	2f	CH_3CN/20-25/15(56), CH_2Cl_2/20-25/12(46), neat/20-25/0.5(99)
1g	2g	CH_3CN/20-25/4(85), CH_2Cl_2/20-25/3(73), neat/20-25/12(55)
1h	2h	CH_3CN/20-25/24(50), CH_2Cl_2/20-25/12(79), neat/20-25/12(78)
1i	2i	CH_3CN/0/2(47)
1j	2j	CH_3CN/0/2(27)
1d	 [a] 3	CH_3CN/20-25/24(60), neat/20-25/12(55)
 1k	 4	neat/0/0.5(73)

[a] 2-Ethoxy-1,3-dithiane was used instead of 2-ethoxy-1,3-dithiolane.

REFERENCES AND NOTES

1. N. K. Kochetkov, E. E. Nifant'ev and V. N. Kulakov, *Doklady Akad. Nauk S. S. S. R.*, 125, 327 (1959); *Chem. Abstr.*, 53, 19873 (1959).
2. E. C. Taylor and J. L. LaMattina, *Tetrahedron Lett.*, 2077 (1977).
3. For acid-catalyzed transformation of 2-ethoxy-1,3-dithiolane see S. Tanimoto, T. Miyake and M. Okano, *Bull. Inst. Chem. Res., Kyoto Univ.*, 55, 276 (1977).
4. All the products in Table 1 (except 2d, 2f and 3) are new compounds. For 2d, 2f and 3, see A. Bargagna, P. Schenone, P. Versace and G. Mallarini, *Pharmacol. Res. Commun.*, 389 (1973); *Chem. Abstr.*, 80, 128318d (1974), ref 1 and 2 respectively.

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