Chinese Chemical Letters Vol. 11, No. 1, pp. 3–4, 2000

Intramolecular Aldol Condensation of α - Oxo Ketene Dibenzylthioacetals：A Facile Route to Substituted Thiophenes

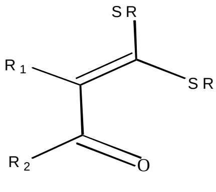
Mang WANG*， Qun LIU，Mei Xing ZHAO，Li Min WANG

Department of Chemistry，Northeast Normal University，Changchun 130024

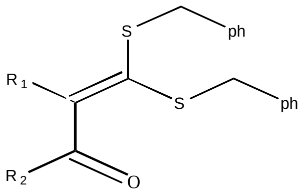
Abstract： A new method for the synthesis of substituted thiophenes was through intramolecular aldol condensation of α-oxo ketene dibenzylthioacetals.All products were confirmed with IR, ^{1}H NMR and elemental analysis.

Keywords： α-Oxo ketene dibenzylthioacetals, substituted thiophenes, intramolecular aldol condensation .

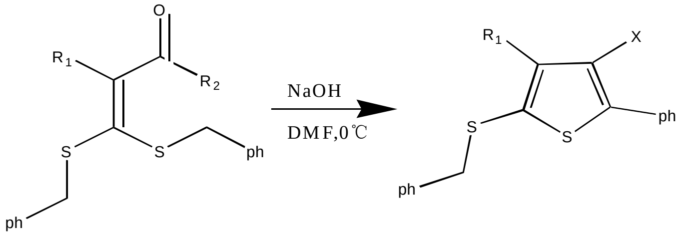
As a kind of intermediates，α-oxo ketene dithioacetals **1** are important in organic synthesis[1,2]. In our recent studies， we found that the difference of dialkythio group can bestow various properties on these kinds of compounds[3,4]. To exploit the reactivity adjusted by the dialkythio groups in **1**，α-oxo ketene dibenzylthioacetals **2** were chosen and studied. Some interesting new results were obtained in these experiments. Here we report the new results.



1



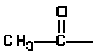
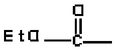
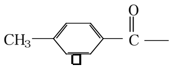
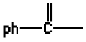
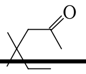
2



2 **3**

When studying the reaction of α-oxo ketene dibenzylthioacetals **2** with sodium alkoxide，we have discovered that compounds **2** can undergo intramolecular aldol condensation to afford substituted thiophenes **3** under mild condition. All products were identified by IR, ^1H NMR and elemental analysis. The yields are listed in **Table 1**.

Table 1. Yield and Elemental analysis of compounds **3**

Entry	R_1	R_2	X	Yield (%)	C (%)	H (%)
3a	 $CH_3-\overset{O}{\overset{\|}{C}}-$	-OEt	-OH	50.0	67.15(67.03)	4.79(4.74)
3b	 $EtO-\overset{O}{\overset{\|}{C}}-$	-OEt	-OH	73.7	64.61(64.84)	4.69(4.90)
3c		$-CH_3$	$-CH_3$	33.7	75.25(75.33)	5.51(5.35)
3d	 $ph-\overset{O}{\overset{\|}{C}}-$	-ph	-ph	55.5	77.70(77.89)	4.55(4.79)
3e	H	$-CH_3$	$-CH_3$	50.3	72.80(72.93)	5.36(5.44)
3f				56.1	72.88(72.98)	5.72(5.86)

A typical procedure（**3b**）: NaOH（4mmol）was added to a solution of α-oxo ketene dibenzylthioacetal（**2b**）in 10ml DMF at 0°C. The mixture was stirred and monitored by TLC for 50 mins.. The reaction was quenched with saturated NH_4Cl（10ml）solution. Dilute HCl was added to acidify the solution to pH=7. Yellow deposit was filtered and purified by crystallization from ethanol. The yield was 73.7%. Elem. Anal. for $C_{20}H_{18}O_3S_2$: Calcd.: C 64.84, H 4.90, Found: C 64.61, H 4.69; IR（KBr）: 3300~2500, 1722; ^1H NMR: δ_H (ppm) 1.40（3H, t, J=7.1, CH_3）, 4.24（2H, s, SCH_2）, 4.40（2H, q, J=7.1, CH_2）, 7.25~7.80（10H, m, ArH）,9.79 (1H, s, OH）; ^{13}C NMR: δ_C (ppm) 14.119 (CH_3), 38.902 (S-CH_2), 61.464 (O-CH_2), 114.013 114.991 (=C-S-C=), 125.711 125.885 127.706 128.457 128.555 129.018 132.447 134.935, 145.609 (C-C=O), 151.526 (C-OH), 165.803 (C=O).

Acknowledgment

This work was supported by Chinese Young Teacher's Foundation of Chinese Education Committee.

References

1. R. K. Dieter, *Tetrahedron*, **1986**, *42*, 3029.
2. H. Junjappa, H. Ila , C. V. Asokan, *Tetrahedron*, **1990**, *46*, 5423.
3. S. Gill, P. Kocienski, A. Kohler, A. Pontiroli, Q. Liu, *J. C. S. chem. Commun.*, **1996**, 1743.
4. Q. Liu, Z. M. Zhu, Z. Y. Yang, Y. Li Hu, F. Y. Jing, Y. W. Xiao, *Chem. J. Chinese Universities*（Chinese）, **1993**, *14*, 1538.

Received 14 May 1999