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Preliminary communication

VO(OR)Cl$_2$-induced cyclization of diketene via ring opening

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Abstract

Diketene undergoes a VO(OR)Cl$_2$-induced cyclization with styrenes via ring opening to give 3-alkoxycarbonyl-2-methyl-5-phenyl-4,5-dihydrofurans. Desilylative aromatization to the furans is observed in the reaction with α-trimethylsilylstyrene.

Redox reactions of transition metals have potential synthetic uses, including the generation of radical species [1]. Pentavalent vanadium compounds are generally considered to be one-electron oxidants [2]. VO(OR)Cl$_2$ has been found to be a versatile Lewis acid in organic media; it can achieve oxidative transformations of carbonyl compounds such as catalytic ring-opening oxygenation [3], dehydrogenative aromatization [4], and decarboxylative deamination [5]. Diketene (**1**) is a useful four-carbon building block in organic synthesis. We here report a novel carbon–carbon bond formation via the VO(OR)Cl$_2$-induced oxidation of diketene.

Diketene was treated with VO(OEt)Cl$_2$ and α-methylstyrene (**2a**) in ethanol giving the ring-enlarged dihydrofuran **3a** (eq. 1) *. Use of more than 2 equiv. of VO(OEt)Cl$_2$ was required to obtain higher yields of **3a** (Table 1). A reaction time of 2 h was sufficient for the formation of **3a**. When the reaction was carried out in dichloromethane or ether a complex mixture resulted. The substituent effect of VO(OR)Cl$_2$ indicates that VO(O^{i}Pr)Cl$_2$ is superior to VO(OEt)Cl$_2$. Styrene (**2c**) underwent a similar cyclization into **3c**–**d**.

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* A typical procedure for the VO(OR)Cl$_2$-induced reaction of diketene with styrenes is as follows. To a solution of VO(OEt)Cl$_2$ (3.0 mmol) in ethanol (3 mL) was dropwise added α-methylstyrene (**2a**, 2.0 mmol) over 15 min at −75 °C under argon. Stirring was continued at the same temperature for 2 h. Diketene (1.0 mmol) was then added dropwise over 15 min to the mixture, which was stirred for 2 h. The mixture was warmed to room temperature and stirred for additional 20 h. Workup was performed by addition of ether and 5% aqueous Na$_2$S$_2$O$_3$ (1 mL). The aqueous layer was extracted with ether, treated with conc. HCl (0.5 mL), and again extracted with ether. The combined organic layers were washed with saturated aqueous NaHCO$_3$ and brine, dried over MgSO$_4$, and concentrated. GLC analysis (2.1 m 10% PEG 20M column, 200 °C) of the residue showed the formation of 3-ethoxycarbonyl-2,5-dimethyl-5-phenyl-4,5-dihydrofuran (**3a**, Table 1).

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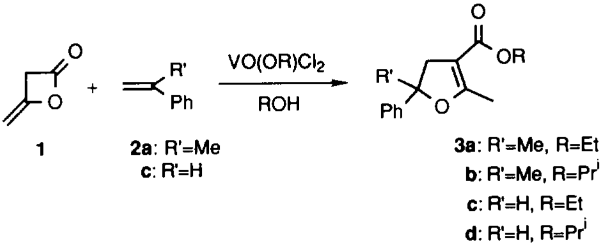
Table 1

VO(OR)Cl_2-induced synthesis of **3**

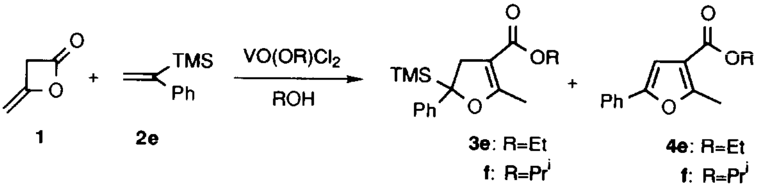
2	equiv.	VO(OR)Cl_2		Solvent	t(h) [a]	**3**	Yield (%)
		R	equiv.				
2a	1	Et	1	EtOH	2	**3a**	14
2a	1	Et	2	EtOH	2	**3a**	32
2a	1	Et	2	EtOH	20	**3a**	34
2a	1	Et	3	EtOH	20	**3a**	45
2a	2	Et	3	EtOH	20	**3a**	47
2a	1	Et	1	Et_2O	2	**3a**	trace
2a	1	Et	2	CH_2Cl_2	2	**3a**	9
2a	1.5	Pr^i	3	Pr^iOH	20	**3b**	73
2c	2	Et	3	EtOH	20	**3c**	32
2c	1.5	Pr^i	3	Pr^iOH	20	**3d**	50

[a] Reaction: −75 °C, 2 h; room temperature, time t, under argon.



(1)

It should be noted that further oxidation occurred when a trimethylsilyl group was present at the α-position of styrene. The VO(OR)Cl_2-induced reaction of **1** with α-trimethylsilylstyrene (**2e**) gave the furan **4** via desilylative aromatization (eq. 2, Table 2). The ratio **4**/**3** could be raised by refluxing the reaction mixture or by treatment under oxygen. This transformation is considered to be due to the oxidation of **3e**–**f** with VO(OR)Cl_2. The isolated dihydrofuran **3e** was oxidized to **4e** in 24% yield on refluxing with 2 equiv. of VO(OEt)Cl_2 in ethanol for 2 h under oxygen.



(2)

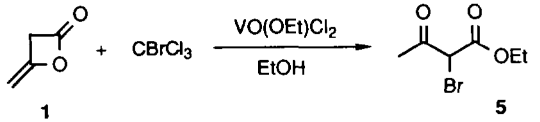
The reaction of **1** with 3 equiv. of VO(OR)Cl_2 in ROH at room temperature for 20 h in the absence of styrenes gave alkyl acetoacetate in a good yield (R = Et, 65%; ^{i}Pr, 81%). Ring opening to alkyl acetoacetate also proceeded in dichloromethane (20% yield), suggesting that VO(OR)Cl_2 participates by introducing an alkoxy group to **3** and **4**. With bromotrichloromethane instead of styrenes in ethanol, selective bromination at the α-position led to the formation of ethyl 2-bromoacetoacetate **5** in 42% yield (eq. 3).

Table 2

VO(OR)Cl$_2$-induced synthesis of **4**

VO(OR)Cl$_2$		t [a] (h)	Product; yield (%)	
R	equiv.			
Et	3	40	**4e** 23	**3e** 43
Et	4	40	**4e** 21	**3e** 54
Et	4	40 [b]	**4e** 37	**3e** 40
Et	4	24 [c]	**4e** 49	**3e** 20
Et	4	24 [d]	**4e** 47	**3e** 44
Pr^i	4	24 [c]	**4f** 52	**3f** 16
Pr^i	4	24 [d]	**4f** 52	**3f** 23

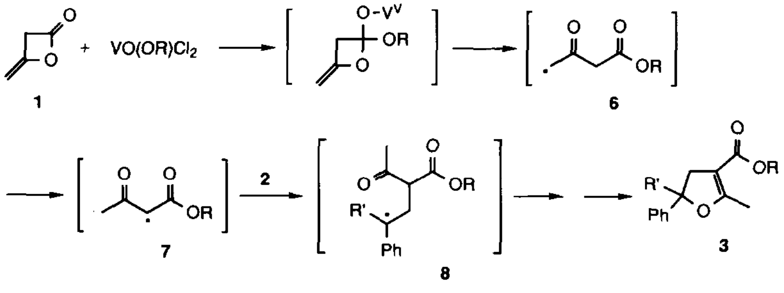
[a] Reaction was carried out at −75°C for 2 h and at room temperature for time t under argon unless otherwise stated. [b] Followed by refluxing for 2 h. [c] Followed by stirring under oxygen at room temperature for 22 h. [d] Followed by stirring under oxygen at room temperature for 4 h and at reflux for 2 h.



(3)

Based on these findings, a similar radical intermediate seems to be involved in the present ring-enlargement reaction as the one proposed in the metal-induced radical reaction of ethyl acetoacetate [6]. A plausible reaction pathway is shown in Scheme 1. The attack of the oxovanadium alkoxide to diketene, followed by ring opening via one-electron oxidation, gives a radical intermediate **6**. The intermediate **6** then isomerizes to the more stable radical **7**, which is capable of forming a new carbon–carbon bond with **2**. Oxovanadium species could form a complex with **7** or with **7** and **2** as reported for Mn$^{\text{III}}$-based oxidation [7]. The interaction with olefin appears to be supported by the VO(OR)Cl$_2$-induced oxidation of α-methylstyrene to acetophenone in the absence of **1** [8]. Cyclization of **8** leads to the dihydrofuran **3**. VO(OR)Cl$_2$ may contribute to desilylative aromatization into **4**, possibly via oxidation of the oxovanadium-dihydrofuran complex.

VO(OR)Cl$_2$ is a versatile one-electron oxidant in oxidative transformations of carbonyl compounds with formation of carbon–carbon bond. Further investigations including the mechanism for oxidative desilylation are now in progress.



Scheme 1

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