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Preliminary communication

VO(OR)Cl₂-induced cyclization of diketene via ring opening

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Abstract

Diketene undergoes a VO(OR)Cl₂-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)Cl₂ 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)Cl₂-induced oxidation of diketene.

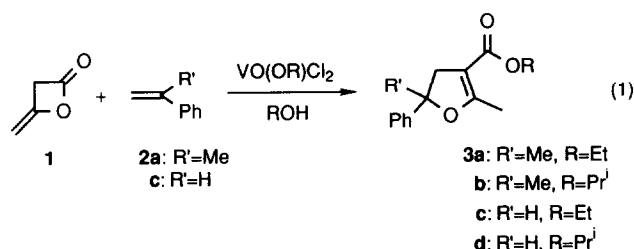
Diketene was treated with VO(OEt)Cl₂ and α -methylstyrene (**2a**) in ethanol giving the ring-enlarged dihydrofuran **3a** (eq. 1) *. Use of more than 2 equiv. of VO(OEt)Cl₂ was required to obtain higher yields of **3a** (Table 1). A reaction time of 2 h was sufficient for the formation of **3a**. When the reaction was carried out in dichloromethane or ether a complex mixture resulted. The substituent effect of VO(OR)Cl₂ indicates that VO(OⁱPr)Cl₂ is superior to VO(OEt)Cl₂. Styrene (**2c**) underwent a similar cyclization into **3c–d**.

* A typical procedure for the VO(OR)Cl₂-induced reaction of diketene with styrenes is as follows. To a solution of VO(OEt)Cl₂ (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 Na₂S₂O₃ (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 NaHCO₃ and brine, dried over MgSO₄, 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).

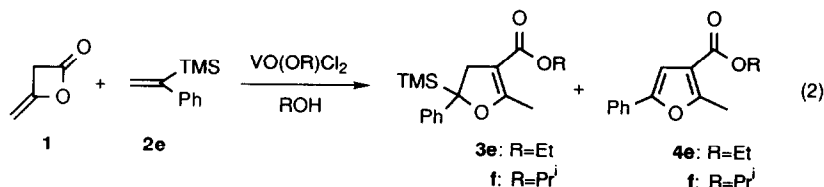
Table 1

VO(OR)Cl₂-induced synthesis of 3

2	equiv.	VO(OR)Cl ₂		Solvent	<i>t</i> (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 ₂ O	2	3a	trace
2a	1	Et	2	CH ₂ Cl ₂	2	3a	9
2a	1.5	Pr ⁱ	3	Pr ⁱ OH	20	3b	73
2c	2	Et	3	EtOH	20	3c	32
2c	1.5	Pr ⁱ	3	Pr ⁱ OH	20	3d	50

^a Reaction: -75 °C, 2 h; room temperature, time *t*, under argon.

It should be noted that further oxidation occurred when a trimethylsilyl group was present at the α -position of styrene. The VO(OR)Cl₂-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)Cl₂. The isolated dihydrofuran 3e was oxidized to 4e in 24% yield on refluxing with 2 equiv. of VO(OEt)Cl₂ in ethanol for 2 h under oxygen.



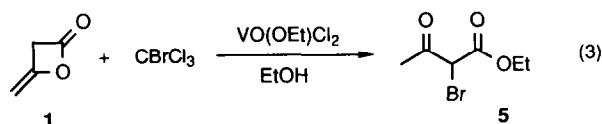
The reaction of 1 with 3 equiv. of VO(OR)Cl₂ in ROH at room temperature for 20 h in the absence of styrenes gave alkyl acetoacetate in a good yield (R = Et, 65%; ⁱPr, 81%). Ring opening to alkyl acetoacetate also proceeded in dichloromethane (20% yield), suggesting that VO(OR)Cl₂ participates by introducing 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)Cl₂-induced synthesis of 4

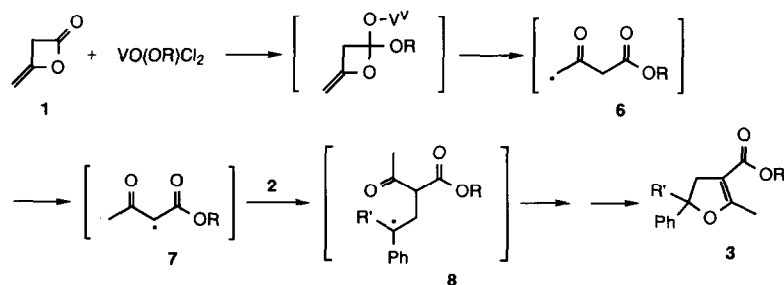
VO(OR)Cl ₂		<i>t</i> ^a (h)	Product; yield (%)			
R	equiv.					
Et	3	40	4e	23	3e	43
Et	4	40	4e	21	3e	54
Et	4	40 ^b	4e	37	3e	40
Et	4	24 ^c	4e	49	3e	20
Et	4	24 ^d	4e	47	3e	44
Pr ⁱ	4	24 ^c	4f	52	3f	16
Pr ⁱ	4	24 ^d	4f	52	3f	23

^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.



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^{III}-based oxidation [7]. The interaction with olefin appears to be supported by the VO(OR)Cl₂-induced oxidation of α -methylstyrene to acetophenone in the absence of 1 [8]. Cyclization of 8 leads to the dihydrofuran 3. VO(OR)Cl₂ may contribute to desilylative aromatization into 4, possibly via oxidation of the oxovanadium-dihydrofuran complex.

VO(OR)Cl₂ 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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