

A stereoselective synthesis of spiro-dioxolanes via the multicomponent reaction of dicarbomethoxycarbene, aldehydes and 1,2- or 1,4-diones

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Abstract—The three component reaction of acyclic carbonyl ylides generated from dicarbomethoxycarbene and aldehydes with 1,2- and 1,4-diones is described. The reaction afforded the corresponding spiro-dioxolanes in good yields.
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1. Introduction

The phenomenal success of the Huisgen 1,3-dipolar cycloaddition reaction in the construction of heterocycles paved the way for the use of unconventional dipoles such as ylides in this reaction. Much of the work in this area, however, has been confined to cyclic carbonyl ylides^{1,2} often generated by the Rh(II) catalyzed decomposition of diazo compounds with suitably positioned carbonyl groups. Imaginative and important applications of cycloadditions involving cyclic carbonyl ylides, especially in the synthesis of natural products, were developed by Padwa and co-workers.³ In contrast, the chemistry of acyclic carbonyl ylides remained largely undeveloped. Our interest in acyclic carbonyl ylides has its origin in our observation that zwitterions generated by the reaction of isocyanides and nucleophilic carbenes with DMAD can be efficiently trapped by carbon heteroatom π bonds leading to the synthesis of highly functionalized heterocycles.⁴

The chemistry of acyclic carbonyl ylides can be traced to the work of Büchner and Curtius who were the first to report the reaction of dicarbomethoxycarbene with carbonyl compounds.⁵ The products of the reaction were characterized as dioxolanes by Dieckmann⁶ in 1910. Later Huisgen and de March investigated the chemistry of carbonyl ylides generated from dicarbomethoxycarbene and carbonyl compounds in detail.⁷ They were able to establish the

intermediacy of carbonyl ylides by trapping it with DMAD. A successful attempt to trap the ylide by a carbon–carbon double bond was reported by Maas⁸ who succeeded in obtaining tetrahydrofuran derivatives by a three component reaction of electrophilic carbene, aldehydes and maleate or fumarate. Recently, Jiang⁹ et al. have reported a stereoselective synthesis of dioxolanes by the 1,3-dipolar cycloaddition reaction of acyclic carbonyl ylides to aldehydes. A stereospecific synthesis of epoxides involving the collapse of the ylides reported by Doyle is also noteworthy.¹⁰

Against this literature background, and in the context of our general interest in the chemistry of 1,2-diones,¹¹ we have explored the reaction of the carbonyl ylides generated from dicarbomethoxycarbene and aldehydes to *o*-quinones. Our preliminary results showing the formation of dioxolanes have already been published.¹² The details of this work along with the results of our extended investigations involving isatins and *p*-quinones are presented in this paper.

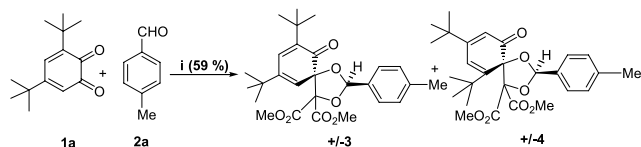
2. Results and discussion

2.1. Reaction with *o*-benzoquinones

Our studies commenced by the Rh(II) catalyzed decomposition of dimethyl diazomalonate in the presence of *p*-tolualdehyde and 3,5-di-*tert*-butyl-1,2-benzoquinone. A facile reaction occurred affording a regioisomeric mixture of dioxolanes **3** and **4** in the ratio 3:1 (Scheme 1).¹²

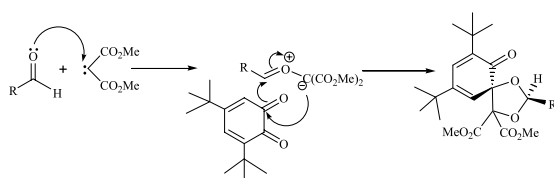
Keywords: Dicarbomethoxycarbene; Carbonyl ylide; Huisgen 1,3-dipolar cycloaddition; Spiro-dioxolane.

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Scheme 1. (i) $\text{N}_2\text{C}(\text{CO}_2\text{Me})_2$, $\text{Rh}_2(\text{OAc})_4$, dry benzene, argon, 80 °C, 14 h.

Mechanistically the reaction may be considered to involve the formation of a carbonyl ylide by the reaction of the carbene and the aldehyde and its trapping by the quinone carbonyls (**Scheme 2**). The diastereoselectivity of the reaction may be rationalized by the concerted nature of the carbonyl ylide cycloaddition and the observed relative stereochemistry of the products may be attributed to the preferred *trans* geometry of the ylide.



Scheme 2.

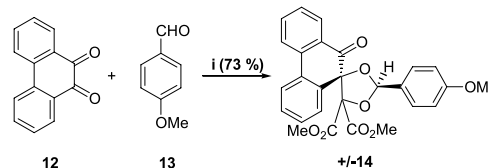
The reaction was found to be general with respect to a variety of aromatic aldehydes, especially those containing electron donating groups, and 1,2-benzoquinones. The dioxolane derivatives were obtained in moderate to good yields. The reaction with 4-*tert*-butyl-1,2-benzoquinone afforded an inseparable mixture of regioisomers in the ratio 1:1. In all cases the structure of the products was established by spectroscopic analysis; IR, ^1H NMR and ^{13}C NMR data were completely consistent with the assigned structure (**Table 1**).

2.2. Reaction with phenanthrene quinone

Subsequent to the above investigations, we examined the addition of acyclic carbonyl ylides to phenanthrenequinone. In a prototype experiment, *p*-anisaldehyde and phenanthrenequinone were exposed to dimethyl diazomalonate in the presence of catalytic amount of Rh(II) acetate in refluxing benzene under an atmosphere of argon for 14 h. The reaction afforded the corresponding dioxolane derivative in 73% yield as a single diastereoisomer (**Scheme 3**).¹²

Table 1.

<i>o</i> -Benzoquinone	Aldehyde	Substituents	Product	Yield (%) / (ratio)
1b	2b	$\text{R}^1=\text{R}^2=\text{C}(\text{CH}_3)_3$, $\text{R}^3=\text{R}^4=\text{R}^5=\text{H}$	5a, 5b	62 (3:1)
1c	2c	$\text{R}^1=\text{R}^2=\text{C}(\text{CH}_3)_3$, $\text{R}^3=\text{R}^5=\text{H}$, $\text{R}^4=\text{OCH}_3$	6a, 6b	40 (3:1)
1d	2d	$\text{R}^1=\text{R}^2=\text{C}(\text{CH}_3)_3$, $\text{R}^3=\text{R}^5=\text{OCH}_3$, $\text{R}^4=\text{H}$	7a, 7b	34 (3:1)
1e	2e	$\text{R}^1=\text{CHPh}_2$, $\text{R}^2=\text{C}(\text{CH}_3)_3$, $\text{R}^3=\text{R}^4=\text{H}$, $\text{R}^5=\text{CH}_3$	8a, 8b	74 (2:1)
1f	2f	$\text{R}^1=\text{CHPh}_2$, $\text{R}^2=\text{C}(\text{CH}_3)_3$, $\text{R}^3=\text{R}^4=\text{R}^5=\text{H}$	9a, 9b	65 (1.4:1)
1g	2g	$\text{R}^1=\text{H}$, $\text{R}^2=\text{C}(\text{CH}_3)_3$, $\text{R}^3=\text{R}^4=\text{H}$, $\text{R}^5=\text{CH}_3$	10a, 10b	41 (1:1)
1h	2h	$\text{R}^1=\text{H}$, $\text{R}^2=\text{C}(\text{CH}_3)_3$, $\text{R}^3=\text{R}^4=\text{R}^5=\text{H}$	11a, 11b	45 (1:1)



Scheme 3. (i) $\text{N}_2\text{C}(\text{CO}_2\text{Me})_2$, $\text{Rh}_2(\text{OAc})_4$, dry benzene, argon, 14 h.

Table 2

Entry	Aldehyde	Products	Yield (%)
1			85
2			78
3			68
4			49

The reaction was extended to a number of other aldehydes; in all cases good yields of the spiro-dioxolane derivatives were obtained and the results are summarized in **Table 2**.

2.3. Reaction with isatins

In the next phase of our studies we extended the reaction to another class of 1,2-dicarbonyl compounds viz. isatins. When *N*-methyl isatin was allowed to react with acyclic carbonyl ylide generated by the reaction of *p*-tolualdehyde

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