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Stereoselective preparation of *Z*-trisubstituted alkyldene cyclic carbonates via palladium-catalyzed carbon–carbon bond formation

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Abstract

Alkyldene cyclic carbonates bearing a *Z*-trisubstituted exocyclic double bond have been stereoselectively prepared in good yields for the first time from methylene cyclic carbonates, resistant to the classical Heck reaction, on treatment with aryl iodides, $\text{CF}_3\text{CO}_2\text{Ag}$ and palladium catalyst, under conditions which tolerate (*sp*²)C–Br bonds. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: palladium catalysis; cyclic carbonates; silver trifluoroacetate.

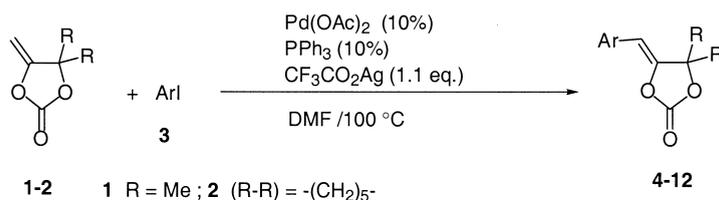
Alkyldene cyclic carbonates are useful intermediates for the easy access to oxazolidinones¹ and β -oxopropyl carbonates and carbamates, and furanone derivatives.² Their activation by palladium or platinum catalysts via oxa- π -allylmetal reactive intermediates makes possible the preparation of a variety of heterocycles upon reaction with aromatic aldehydes,³ isonitriles and heterocumulenes,⁴ as well as ketonic cyclopropanes on reaction with norbornene.⁵ More importantly, enantioselective hydrogenation of α -methylene cyclic carbonates in the presence of ruthenium catalysts has led to the obtention of optically active bicyclic carbonates and 1,2-diols with very high enantioselectivities.⁶ This observation motivated the search for alkyldene cyclic carbonates as new intermediates towards optically active compounds.

The most straightforward syntheses of α -methylene cyclic carbonates are based on the condensation of propargylic alcohols with carbon dioxide in the presence of ruthenium,⁷ cobalt,⁸ copper,⁹ phosphine,¹⁰ or strong base¹¹ catalysts. The only two efficient methods to produce trisubstituted alkyldene cyclic carbonates are the palladium-catalyzed coupling of propargylic

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alcohol, CO₂ and vinyl or aryl halide,¹² and rearrangement of allyl propargyl carbonates.¹³ Both methods stereoselectively afford the *E*-trisubstituted exocyclic double bond.

Whereas the classical Heck type reaction applied to methylene cyclic carbonates **1–2** does not allow the access to alkylidene carbonates, we now report the first stereoselective synthesis of *Z*-trisubstituted alkylidene cyclic carbonates in good yields from **1** or **2**, aryl iodides and CF₃CO₂Ag in the presence of palladium catalyst according to Scheme 1.



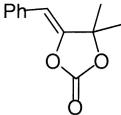
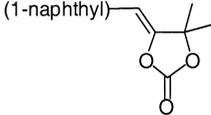
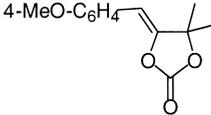
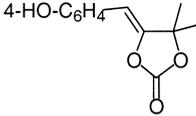
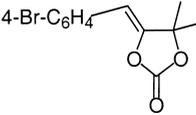
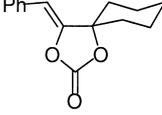
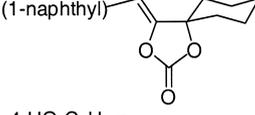
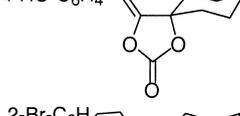
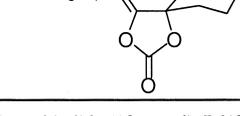
Scheme 1.

The treatment of the α -methylene cyclic carbonate **1** with iodobenzene under classical palladium-catalyzed C–C coupling conditions in the presence of Et₃N or K₂CO₃ as a base and even with Bu₄NBr or AgNO₃ as promoter¹⁴ did not lead to any transformation.

The key point of the success of the C–C coupling reaction is the presence of a stoichiometric amount of CF₃CO₂Ag. Thus, the treatment of 1.50 g (11.7 mmol) of 4,4-dimethyl-5-methylen-1,3-dioxolan-2-one **1**¹⁰ with 2.45 g (12 mmol) of iodobenzene **3** and 3.24 g (14.6 mmol) of silver trifluoroacetate in the presence of 90 mg (1.2 mmol-10 mol%) of palladium acetate, 312 mg (1.2 mmol, 10 mol%) of triphenylphosphine in 8 ml of DMF at 100°C for 20 h led to a complete conversion into 5-benzylidene-4,4-dimethyl-1,3-dioxolan-2-one. The crude mixture contained a mixture of *Z*- and *E*-isomers in the ratio *Z/E* = 95/5, and after workup and chromatography over silica gel, the pure *Z*-isomer **4** (R=Ph) was isolated as white crystals in 87% yield (2.10 g). The presence of CF₃CO₂Ag is crucial in this reaction as neither CF₃CO₂Na nor CH₃CO₂Ag used in stoichiometric amounts were active to promote the C–C coupling, showing that the presence of both trifluoroacetate and silver was necessary. The stereochemistry of the exocyclic double bond was attributed due to the olefinic proton shift in ¹H NMR by comparison with the literature data (*E*-isomer: $\delta_{\text{H}} = 6.40$ ppm^{12b}; *Z*-isomer: $\delta_{\text{H}} = 5.48$ ppm).

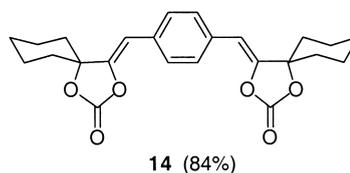
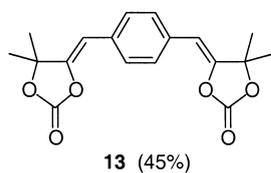
Under the experimental conditions reported in Scheme 1, the coupling of a variety of aryl iodides with carbonates **1** and **2** was performed (Table 1). The coupling reaction appeared to be quite general as phenyl and 1-naphthyl *Z*-substituted cyclic carbonates were isolated in good yields from carbonates **1** and **2** (Table 1, entries 1, 2, 6, 7). The reaction tolerated the presence of functionalities and 4-hydroxybenzylidene substituted carbonates **7**, **11** were prepared in satisfactory yields from the corresponding iodides (entries 4, 8). However, no reaction took place from 1-amino-4-iodobenzene and 4-nitroiodobenzene. This coupling reaction was specific of aryl iodides because aryl bromides, which are usually suitable substrates for the Heck coupling, were unreactive. This observation made possible the preparation, from the corresponding bromiodobenzene, of 2- and 4-bromobenzylidene cyclic carbonates **8** and **12** (entries 5, 9), which are interesting substrates for further classical Heck reactions involving the activation of C–Br bond. The role of silver trifluoroacetate might be in the capture of iodide from the oxidative addition product L_nPd(Ar)(I), allowing the coordination of non-reactive C=C bonds.¹⁵

Table 1
Coupling of aryl iodides with carbonates **1** and **2**^a

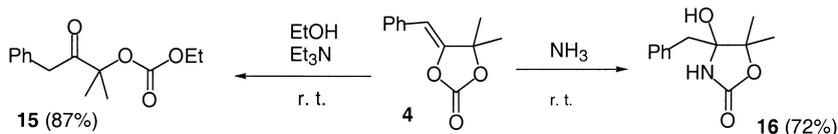
entry	carbonate	aryl iodide	product	yield (%)
1	1	iodobenzene		4 87
2	1	1-iodonaphthalene		5 40
3	1	4-iodoanisole		6 51
4	1	4-iodophenol		7 35
5	1	1-bromo-4-iodobenzene		8 60
6	2	iodobenzene		9 86
7	2	1-iodonaphthalene		10 41
8	2	4-iodophenol		11 67
9	2	1-bromo-2-iodobenzene		12 53

^a General conditions : methylene carbonate (10 mmol), aryl iodide (10 mmol), Pd(OAc)₂ (1 mmol), PPh₃ (1 mmol), CF₃CO₂Ag (11 mmol), DMF (8 ml), 100 °C, 20 h.

The new *Z,Z*-biscarbonates **13** and **14** were also prepared from 1,4-diiodobenzene and carbonates **1** and **2** in 45 and 84% isolated yield, respectively.



The reactivity of this new family of *Z*-alkylidene cyclic carbonates showed their straightforward transformation into acyclic ketocarbonates and hydroxyoxazolidinones upon reaction with a nucleophile in the presence of a base (Scheme 2). Thus, the treatment of **4** with ethanol used as a solvent in the presence of Et₃N at room temperature gave 1,1-dimethyl-3-phenyl-2-oxopropyl ethyl carbonate **15** in 87% isolated yield. Similarly, the obtention of the hydroxyoxazolidinone **16** resulted from the quantitative conversion of carbonate **4** (72% isolated yield) upon treatment with ammonia in diethyl ether at room temperature.



Scheme 2.

The crucial action of silver trifluoroacetate in the palladium-catalyzed carbon–carbon bond formation from the exocyclic double bond of methylene cyclic carbonates has thus removed the inhibition to perform the Heck type reaction. It provides an easy access not only to substituted alkylidene cyclic carbonates but also to high *Z*-stereoselectivity. Biscarbonates such as **13** and **14** are potential precursors of polymers containing β -ketocarbonate units in the main chain and according to the observed highly enantioselective catalytic hydrogenation of **1**,⁶ these compounds **4–14** should open the route to a variety of optically active useful derivatives.

Acknowledgements

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