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α-Methylene Cyclic Carbonate as a Conjunctive Agent for Aromatic Aldehydes

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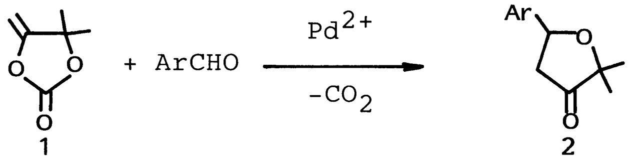
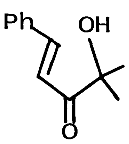
α-Methylene cyclic carbonate underwent decarboxylative cycloaddition to aromatic aldehydes to yield dihydrofuranone derivatives in the presence of a dicationic palladium complex.

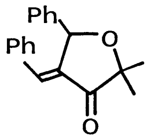
Five-membered methylene carbonates are prepared conveniently from α-ethynyl alcohols and CO_2.[1)] They bear vinyl ether and protected allylic alcohol moieties and have been anticipated to serve as potential precursors for conjunctive agents.[2)] Here we report a decarboxylative cycloaddition reaction of 4,4-dimethyl-5-methylene-1,3-dioxolan-2-one (**1**) to aromatic aldehydes to produce dihydrofuranone derivatives **2** assisted by a dicationic palladium complex, $[Pd(CH_3CN)_4](BF_4)_2$ (3).[3)]



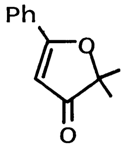
Heating a neat mixture of **1** (5 mmol) and benzaldehyde (15 mmol) with 10% complex 3 at 70 °C for 2 h under N_2 atmosphere gave 2,2-dimethyl-5-phenyldihydrofuran-3-one (**2a**; Ar=Ph), which was isolated by column chromatography (silica gel/chloroform) in 63% yield. A monocationic complex, $[Pd(acac)(cod)](BF_4)$, a zerovalent complex, $[Pd(PPh_3)_4]$, and various the other transition metal-BF_4 dicationic complexes including those of Fe, Co, Ni, Pt, Cu, and Zn were less active catalysts affording **2a** in 0-6% yields. The dioxolanone **1** reacted similarly with several aromatic aldehydes to produce the corresponding dihydrofuranones **2** in moderate to modest yields: 38% from $4\text{-}CH_3C_6H_4CHO$, 57% from $4\text{-}ClC_6H_4CHO$, trace from $4\text{-}CH_3OC_6H_4CHO$, 38% from 1-naphthaldehyde. Unfortunately, heteroaromatic, aliphatic, or olefinic aldehydes (furfural, nicotinic aldehyde, butanal, chloral, 3-cyclohexene-1-carboxaldehyde, cinnamaldehyde) did not participate in this reaction. The reaction of **1** with benzaldehyde took place analogously in the presence of a Lewis acid such as $ZnCl_2$ or $AlCl_3$. In this case, however, the formation of **2a** was usually accompanied by that of **4a** and/or **5a**. For example, **1** (10 mmol) and benzaldehyde (10 mmol) were reacted at 100 °C for 2 h in the presence of $ZnCl_2$ (4 mmol) to produce **2a** (13%), **4a** (26%), and **5a** (19%).



4a



5a



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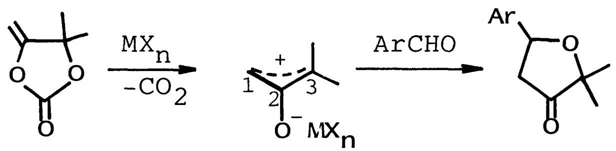

A tentative mechanism involves a bidentate 1,3-dipolar intermediate **6**$^{4)}$ generated in situ decarboxylatively, where the $C_1C_2C_3$ group should be electrophilic and the C_1C_2O group should be nucleophilic. This would cycloadd to an aromatic aldehyde to give the dihydrofuranone **2**. The regioselectivity of the cycloaddition can be interpreted in terms of the greater positive charge on the C_3 carbon. The synthetic utility of **2a** has been proved by the facile preparation of a natural product, bullatenone (**7**), via oxidation with SeO_2.$^{5)}$

This reaction provides a new methodology to generate the reactive species **6** which is useful as a three carbon unit.

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