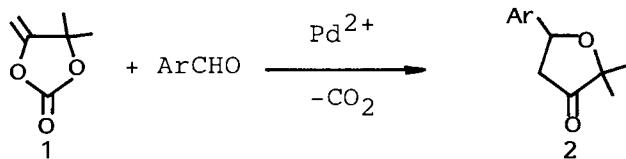


α -Methylene Cyclic Carbonate as a Conjunctive Agent for
Aromatic Aldehydes

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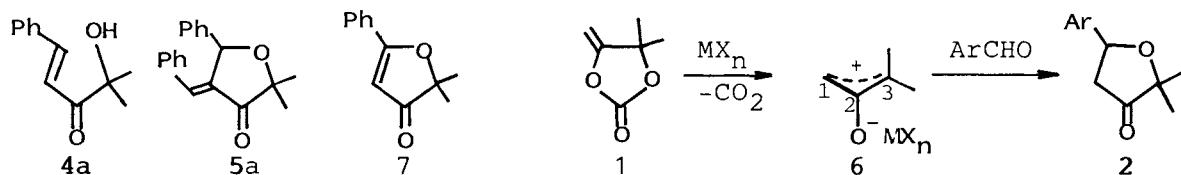
α -Methylene cyclic carbonate underwent decarboxylative cycloaddition to aromatic aldehydes to yield dihydrofuranone derivatives in the presence of a dicationic palladium complex.

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, $[\text{Pd}(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$ (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, $[\text{Pd}(\text{acac})(\text{cod})](\text{BF}_4)$, a zerovalent complex, $[\text{Pd}(\text{PPh}_3)_4]$, 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 $4-\text{CH}_3\text{C}_6\text{H}_4\text{CHO}$, 57% from $4-\text{ClC}_6\text{H}_4\text{CHO}$, trace from $4-\text{CH}_3\text{OC}_6\text{H}_4\text{CHO}$, 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%).



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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