Tetrahedron Letters, Vol.32, No.44, pp 6315-6318, 1991
Printed in Great Britain

0040-4039/91 $3.00 + .00
Pergamon Press plc

Synthesis of Allylic Aryl Ethers via Palladium-Catalyzed Decarboxylation of Allylic Aryl Carbonates

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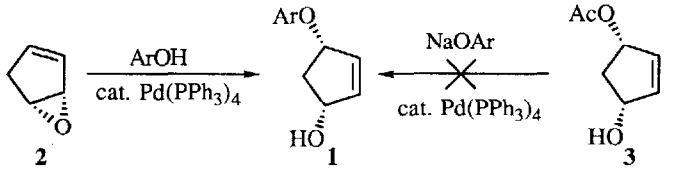
Key Words: allylic aryl ethers; allylic aryl carbonates; palladium-catalyzed decarboxylation

Abstract: *Allylic aryl ethers are readily prepared in high yield by the palladium-catalyzed decarboxylation of allylic aryl carbonates.*

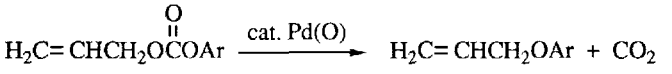
Allylic aryl ethers are very valuable in organic chemistry, particularly as substrates for the Claisen rearrangement.[1] Our recent work on the synthesis of benzoprostacyclins required the preparation of an allylic aryl ether of the type **1** where the aryl group contained two bulky *ortho* substituents.[2] While the desired substrate could be obtained in racemic form from cyclopentadiene monoepoxide (**2**), an attempt to prepare it in chiral form via the corresponding hydroxy acetate **3** failed completely (eq. 1). This was surprising since



(1)

aryloxides have previously been utilized as nucleophiles in π-allylpalladium chemistry[3] and this exact conversion had previously been accomplished in 90% yield using sodium phenoxide.[3g] No improvement was observed after several variations in the original reaction conditions. Our lack of success was presumably due to the increased steric hindrance of our nucleophile and the resulting reluctance of the *intermolecular* displacement to take place.

We reasoned that an *intramolecular* variation might prove more successful and chose to examine the palladium-catalyzed decarboxylation of allylic aryl carbonates (eq. 2). While allylic carbonates are known to be



(2)

more reactive than allylic acetates in π-allylpalladium chemistry,[4] their only reported chemistry with oxygen nucleophiles involves their palladium-catalyzed hydrogenolysis to alkenes[5] and one example of the decarboxylation of allyl benzyl carbonate to allyl benzyl ether.[5a] We have examined the generality of this latter process using allylic aryl carbonates and wish now to report that it is a valuable new route to allylic aryl ethers.

Allylic phenyl carbonates were readily prepared by coupling the appropriate allylic alcohol and phenyl chloroformate (eq. 3). The yields ranged from 50-100%, with the typical yield being greater than 90%.

$$H_2C{=}CHCH_2OH \xrightarrow[1.5\ \text{pyridine}]{1.2\ ClCO_2Ph} H_2C{=}CHCH_2O\overset{\overset{O}{\|}}{C}Ph \qquad (3)$$

benzene

Unfortunately, no general method for the synthesis of other allylic aryl carbonates was available, but we have developed such a process using triphosgene (eq. 4).[6] The following procedure is representative. To a

$$ArOH \xrightarrow[2.\ 1\ \text{allylic alcohol, 1}\ C_5H_5N]{1.\ 0.4\ Cl_3COCO_2CCl_3,\ 1\ C_5H_5N} \text{allylic aryl carbonates} \qquad (4)$$

solution of the phenol (20 mmol) and triphosgene (2.3 g, 7.2 mmol) in 40 ml of CH_2Cl_2 was added pyridine (1.6 g, 20 mmol) dropwise at room temperature. The resulting mixture was stirred for 30 min at that temperature and the allylic alcohol (20 mmol) was then added, followed by pyridine (2.0 g, 25 mmol). After the reaction mixture was stirred for 2 h, it was quenched by adding 20 ml of H_2O, and the organic phase was separated, dried, concentrated and purified by flash chromatography. Yields range from 71-90%.

In examining the subsequent decarboxylation process, 1.5-5 mol % $Pd(PPh_3)_4$ as catalyst worked reasonably well on some substrates, but the combination of 5 mol % $Pd(OAc)_2$ and 20 mol % PPh_3 proved superior overall, especially with sterically hindered substrates. Best results were obtained using THF or CH_2Cl_2 as the solvent and running the reactions at 25-50 °C for anywhere from 1 hour to 3 days, the reaction time apparently depending on the degree of steric hindrance about the carbon-carbon double bond.

The following procedure is representative of that used. To a flask were added the allylic aryl carbonate (1.0 mmol), PPh_3 (52.4 mg, 0.2 mmol), $Pd(OAc)_2$ (11.2 mg, 0.05 mmol) and THF or CH_2Cl_2 (20 ml). The resulting mixture was stirred at the appropriate temperature until the reaction was judged complete by TLC analysis, concentrated using a rotary evaporator, and purified by flash chromatography. Our results are summarized in Table 1.

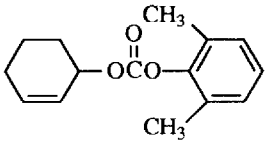
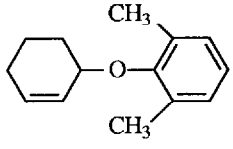
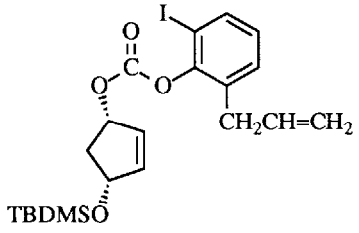
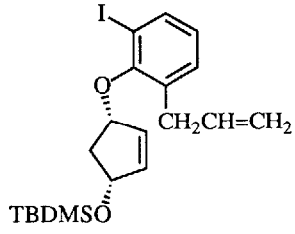
The decarboxylation process works well for a variety of carbonates containing 1°, 2° and 3° allylic groups and even hindered aromatic groups (see entries 8 and 9). Allylic rearrangements consistent with the intermediacy of a π-allylpalladium species are observed. Identical mixtures are obtained from regioisomeric allylic carbonates (compare entries 3 and 4, and 5 and 6). The more highly substituted ether product tends to predominate, except where conjugation stabilizes the product (entry 7). Where steric effects at the allylic termini are substantially different (see entries 5, 6 and 9), a single isomeric product is observed.

Mechanistically, the process is observed to proceed with overall retention of configuration (entry 9). Since allylic esters are known to react with palladium(0) by an inversion process to form π-allylpalladium species, aryloxide attack on this intermediate must be proceeding with inversion. Substitution at the more substituted allylic termini is typical of oxygen nucleophiles[3] and quite different from nitrogen and carbon nucleophiles. It is noteworthy that both a carbon-carbon double bond and an aryl iodide moiety can be accommodated by this process (see entry 9).

Synthetically, this process provides a valuable new route to allylic aryl ethers. It should be particularly useful for the synthesis of ethers bearing sterically hindered allylic or aryl substituents, such as 1,1-dimethylallyl aryl ethers so widely used in the synthesis of isopentenyl natural products.[7] It would appear to accommodate the wide variety of functional groups typical of organopalladium chemistry.

Acknowledgment. We gratefully acknowledge the American Heart Association - Iowa Affiliate for financial support of this research and Johnson Matthey, Inc. and Kawaken Fine Chemicals, Ltd. for supplying the palladium acetate.

Table 1. Synthesis of Allylic Aryl Ethers

Entry	Substrate	Reaction Conditions[a]	Product(s)[b]	% Isolated Yield (ratio)
1	$H_2C{=}CHCH_2OCO_2Ph$	1 h, 25 °C, THF	$H_2C{=}CHCH_2OPh$	87
2	$H_2C{=}C(CH_3)CH_2OCO_2Ph$	4 h, 25°C, THF	$H_2C{=}C(CH_3)CH_2OPh$	81
3	*E*- $CH_3CH{=}CHCH_2OCO_2Ph$	1 h, 50 °C, THF	$H_2C{=}CHCH(CH_3)OPh$ (**3**) + *E*- $CH_3CH{=}CHCH_2OPh$ (**4**)	74 (86:14)
4	$H_2C{=}CHCH(CH_3)OCO_2Ph$	2 h, 25 °C, THF	**3** + **4**	80 (86:14)
5	$(CH_3)_2C{=}CHCH_2OCO_2Ph$	1 d, 25 °C, CH_2Cl_2	$H_2C{=}CHC(CH_3)_2OPh$ (**5**)	42[c]
6	$H_2C{=}CHC(CH_3)_2OCO_2Ph$	5 h, 25 °C, THF	5	60
7	*E*- $PhCH{=}CHCH_2OCO_2Ph$	5 h, 25 °C, THF	*E*- $PhCH{=}CHCH_2OPh$ + $H_2C{=}CHCH(Ph)OPh$	89 (89:11)
8		3 d, 25 °C, CH_2Cl_2		74
9		1 d, 25 °C, THF		55 (61)[d]
10	$(CH_3)_2C{=}CHCH(CH_3)OCO_2Ph$	2 d, 50 °C, THF	*E*- $CH_3CH{=}CHC(CH_3)_2OPh$ + $(CH_3)_2C{=}CHCH(CH_3)OPh$	43 (53)[d,e] (60:40)

[a] All reactions were run under nitrogen using 5 mol % $Pd(OAc)_2$, 20 mol % PPh_3, 1.0 mmol of substrate in 20 ml of solvent for the indicated time and temperature unless otherwise indicated.

[b] All products gave the expected ^1H and ^{13}C NMR, IR and mass spectral or combustion analysis data.

[c] An additional portion of catalyst [5% $Pd(OAc)_2$ and 20% PPh_3] was added after 12 h.

[d] The yield in parenthesis is based on recovered starting material.

[e] This reaction employed 5 mol % $Pd(PPh_3)_4$ as catalyst.

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(Received in USA 24 July 1991)