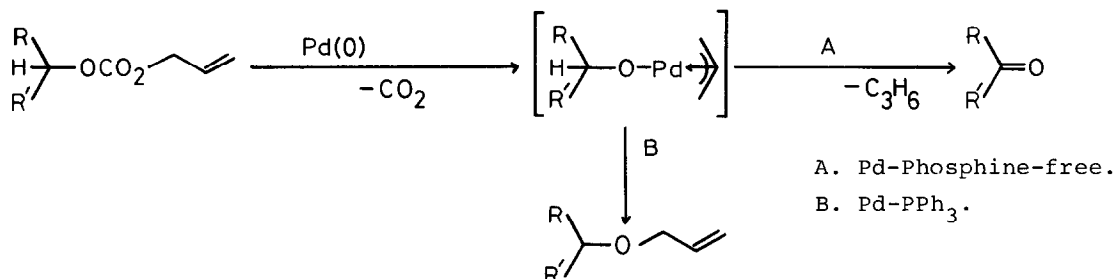


**PALLADIUM-CATALYZED OXIDATION OF ALCOHOLS VIA THEIR
ALLYL CARBONATES UNDER NEUTRAL CONDITIONS**

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Summary: Treatment of alkyl allyl carbonates derived from various alcohols with a palladium catalyst in MeCN affords ketones and aldehydes in high yields. This new method of oxidation of alcohols can be applied to various alcohols except simple primary alcohols.

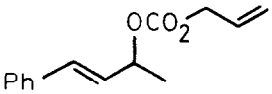
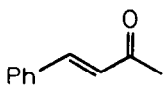
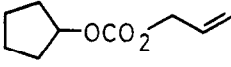
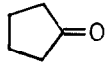
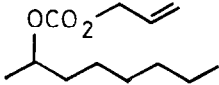
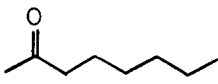
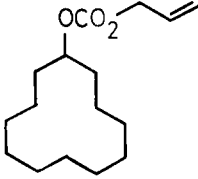
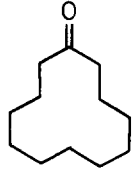
Oxidation of alcohols to the corresponding ketones and aldehydes is one of the most important synthetic methods. A number of oxidation methods are known, mainly by using inorganic reagents such as Cr and Mn salts, and the separation of inorganic compounds is sometimes a problem.¹⁾ We now wish to report a new method of palladium-catalyzed oxidation of alcohols via their allyl carbonates, which are prepared easily by the reaction of alcohols with allyl chloroformate. As expressed by the following scheme, the reaction produces only CO₂ and propene as by-products, and hence the reaction is very clean.



As shown in the table, the reaction can be applied to various alcohols except simple primary alcohols, which give somewhat lower yields, and a considerable amount of alcohols is recovered (entry 4). The phosphine-free palladium is an active catalyst. In the presence of PPh₃, the decarboxylation-ether formation takes place without undergoing the oxidation.²⁾ When unsymmetrical biallylic carbonates are subjected to the oxidation, (entries 2, 3, and 5), the less hindered simple allyl group is cleaved to form α, β -unsaturated ketones or aldehydes.

Several types of palladium-catalyzed oxidation of alcohols are known.³⁻⁵⁾ Only the allyl carbonate method reported in this paper can be carried out under neutral conditions.

Table^{a)}

Entry	Allyl Carbonate	Product	Yield ^{b)}
1	<chem>PhCH2OCO2CH2CH=CH2</chem>	<chem>PhCHO</chem>	76%
2	<chem>nC3H7CH=CHCH2OCO2CH2CH=CH2</chem>	<chem>nC3H7CH=CHCHO</chem>	(95%)
3	<chem>PhCH=CHCH2OCO2CH2CH=CH2</chem>	<chem>PhCH=CHCHO</chem>	69%
4	<chem>nC10H21OCO2CH2CH=CH2</chem>	<chem>nC9H19CHO</chem> <chem>nC10H21OH</chem>	(27%) (73%)
5			88%
6			(76%)
7			(96%)
8			77%

a) Reaction Conditions; Allylic carbonate (1 mmol), Pd(OAc)₂ (0.1 mmol), dry MeCN (5 cm³) at 80 °C for 1-2 h under argon. b) Isolated yields, GLC yields in parenthesis.

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