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A General Synthetic Method for α-Methylene Compounds by the Palladium-Catalyzed Decarboxylation-Deacetoxylation of Allyl α-Acetoxymethylcarboxylates Substituted by an Electron-Withdrawing Group at α-Position#

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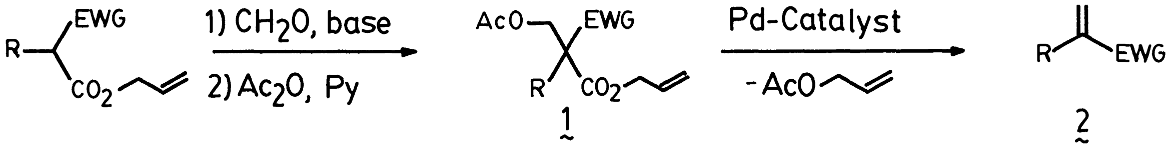
Allyl α-acetoxymethylcarboxylates substituted by ester, amide, nitro, cyano, and sulfonyl groups at α-position undergo smooth palladium-catalyzed decarboxylation-deacetoxylation under mild neutral conditions to afford corresponding α-methylene compounds in high yields.

α-Methylene compounds are reactive intermediates useful for various organic synthesis. Particularly, α-methylene-γ-lactone is an important functional group present in some natural products which have interesting biological activity. Considerable synthetic studies on these functional groups have been carried out.$^{1)}$ We now wish to report a general synthetic method for α-methylene compounds under mild neutral conditions by the palladium-catalyzed decarboxylation-deacetoxylation of allyl α-acetoxymethylcarboxylates substituted by an electron withdrawing group (EWG) at α-position. The reaction can be expressed by the following general scheme.



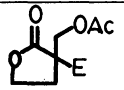
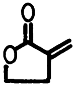
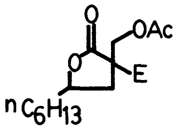
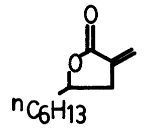
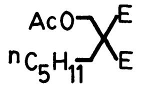
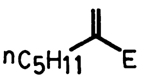
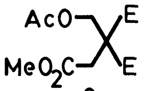
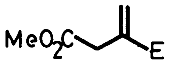
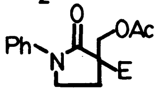
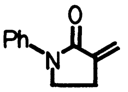
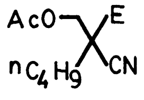
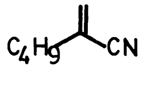
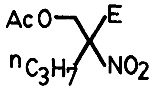
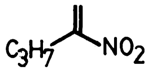
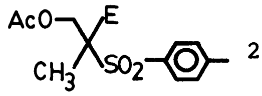
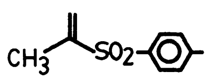
EWG = $-CO_2R$, $-CONR_2$, $-NO_2$, $-SO_2R$, $-CN$, $-C(O)R$.

In our continuing studies on the palladium-catalyzed reactions of allyl β-keto carboxylates, we have found that α-methylene ketones can be prepared in high yields with good selectivity from allyl α-acetoxymethyl-β-keto carboxylates.$^{2)}$ Based on mechanistic consideration on this reaction, we expected that the reaction should be extended to any allyl α-acetoxymethylcarboxylates which have an electron-withdrawing group at α-position. We were pleased to find that various electron-withdrawing groups such as ester, amide, nitro, cyano, and sulfonyl groups are capable of undergoing the expected reaction under mild conditions. Results of the reaction with several substrates are shown in <Table 1>. Generally, the reaction was carried out by the following procedure. A solution of **1** (1 mmol), $Pd_2(dba)_3 \, CHCl_3$ (0.025 mmol), and PPh_3 (0.1 mmol) in dry MeCN (5 cm^3) was stirred for 15 min under argon. After the reaction was complete, the α-methylene compound **2** was isolated by column chromatography on silica-gel.

Dedicated to Professor T. Mukaiyama on the occasion of his 60th birthday.

The present reaction proceeds smoothly at moderate temperatures without using base or acid. Therefore, no isomerization of unstable exomethylene group took place during the reaction and no isomers were detected by TLC and GLC analyses. Since the allyl acetoxymethylcarboxylates can be prepared easily by the acetoxymethylation with formaldehyde and acetic anhydride, the present reaction offers a convenient general synthetic method for various α-methylene compounds, including exomethylene-γ-lactones.

Table 1. Preparation of α-Methylene Compounds

Run	Substrate	Temp/°C	Product	Yield/%
1		50		74
2		50		93
3		40		87
4		40		83
5		80		87
6		25		96#
7		25		74#
8		25		89

$E = CO_2CH_2CH=CH_2$

Calculated by GLC analysis

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