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PALLADIUM-CATALYZED [3 + 2] CYCLOADDITION REACTION USING 2-(SULFONYLMETHYL)- OR 2-(CYANOMETHYL)ALLYL CARBONATE

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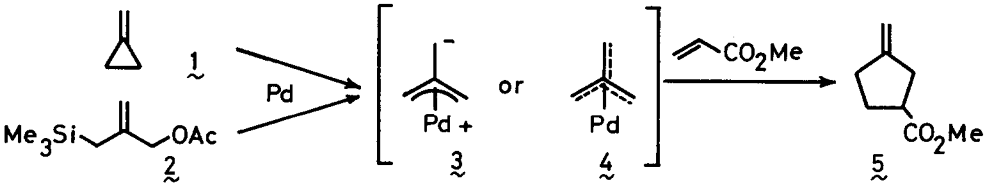
Summary: Reaction of ethyl 2-(sulfonylmethyl)- or 2-(cyanomethyl)allyl carbonate with α,β-unsaturated esters or ketones in the presence of $Pd_2(dba)_3.CHCl_3$-dppe catalyst gave highly functionalized cyclopentanes regioselectively in good yields.

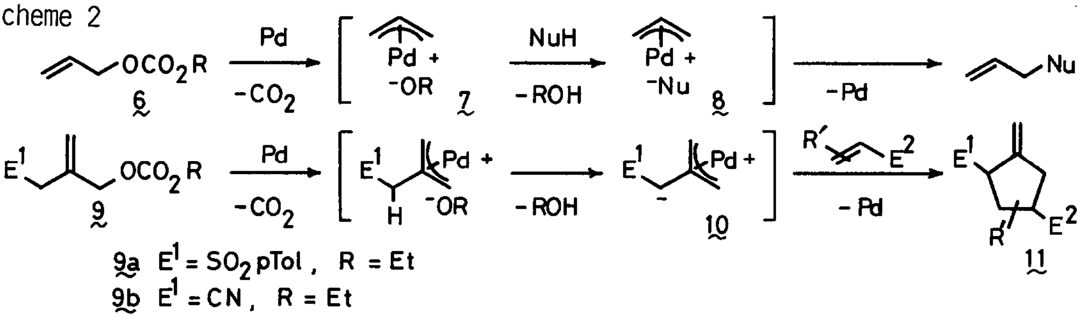
Efficient synthesis of cyclopentanoids is a current interest, and numerous methods have been reported.1) Most of them require multistep procedures for the construction of cyclopentane systems, and good direct methods are rather rare.2) As one method of the direct preparation of cyclopentanes, 1,3-dipolar cycloaddition is very useful. Among several possibilities of the cycloaddition, palladium-catalyzed [3 + 2] cycloaddition reactions using methylenecyclopropane (**1**) and 2-(trimethylsilylmethyl)allyl acetate (**2**) to form methylenecyclopentanes **5** have been reported.3-5) (Scheme 1) The zwitter ionic complex **3** or palladium trimethylenemethane complex **4** is known as an active intermediate in the reaction of **1** and **2**. The usefulness of these methods in organic synthesis depends upon easy accessibility of starting materials with various functional groups.6)

Scheme 1



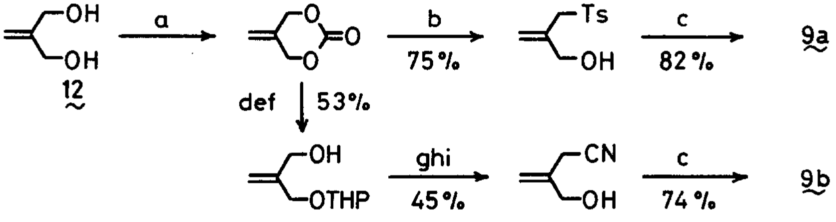
We have reported that oxidative addition of allylic carbonates **6** to Pd(0), followed by decarboxylation generates π-allylpalladium alkoxides **7** as intermediates. Alkoxide anion of the complexes **7** acts as a base to pick up acidic hydrogen from carbonucleophiles to form carbanions, and the catalytic allylation of carbonucleophiles under neutral conditions is possible.7) These results suggested us the zwitter ionic π-allylpalladium intermediates bearing electron withdrawing groups **10** can be obtained from **9**. In this paper, we wish to report palladium catalyzed [3 + 2] cycloaddition reactions using ethyl 2-(sulfonylmethyl)- or 2-(cyanomethyl)allyl carbonates and α,β-unsaturated esters or ketones to give highly functionalyzed cyclopentanes **11** regioselectively.

Scheme 2



Allylic carbonates **9a** and **9b** were prepared from the cyclic carbonate of 2-methylene-1,3-propanediol (**12**) by the following procedure.

Scheme 3

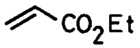
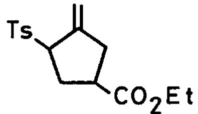
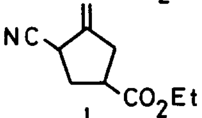
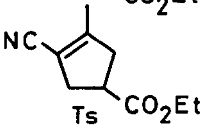
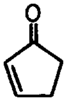
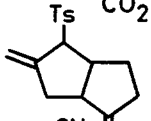
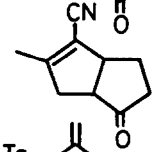
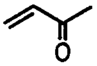
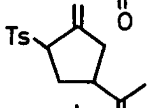
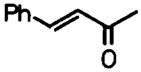
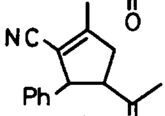
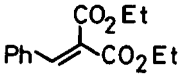
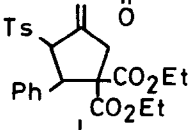
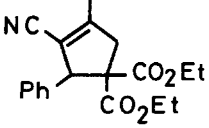


a. $ClCO_2CCl_3$, Et_3N, Et_2O. b. $TsNa.4H_2O$, Pd(0)-PPh_3, THF-MeOH. c. $ClCO_2Et$, pyridine, Et_2O. d. AcOH, Pd(0)-PPh_3, THF. e. DHP, TsOH, CH_2Cl_2. f. K_2CO_3, MeOH. g. PPh_3, CCl_4. h. KCN, 18-Crown-6, MeCN. i. TsOH, MeOH.

Reaction of **9a** (0.5 mmol) and ethyl acrylate (1.0 mmol) in the presence of $Pd_2(dba)_3.CHCl_3$-dppe (1 : 4, 0.0125 mmol) in THF (5 mL) at 65 °C for 20 h gave methylenecyclopentane **13** in 77% yield after purification by column chromatography on SiO_2. Other examples of cyclopentane synthesis using **9a** and **9b** with α,β-unsaturated esters and ketones are listed in Table 1. Various five membered cyclic compounds were obtained in good yields. α-Cyanomethylenecyclopentane **14** was obtained in 66% yield by the reaction of **9b** with ethyl acrylate. However, in the reaction of **9b**, exo-olefins of the adducts were isomerized to stable internal olefins after a longer period of reactions. Reaction of **9a** and **9b** with 2-cyclopentenone gave bicyclo[3.3.0]octane **16** and -octene **17** in 65% and 71% yields.

A variety of cyclopentane derivatives can be derived from the adduct **13**, which has useful functional groups, and various transformations of the functional groups and regioselective carbon-carbon bond formation on **13** are possible. Several examples of the transformation of **13** are shown in Scheme 4. Ozonolysis of exomethylene of **13** gave α-sulfonylcyclopentanone **22**. The sulfone of **13** was removed without isomerization of olefin to give **23** by Pd(0)-PBu^n_3 catalyzed hydrogenolysis with ammonium formate.[8] Regioselective palladium catalyzed allylation was carried out with allyl ethyl carbonate under neutral conditions to give **24**.[7] Allylic rearrangement of sulfone of **13** to **25** was performed using Pd(0)-dppe catalyst in refluxing CH_3CN for 20 h.[9] The isomeric allylic sulfone **25** was also obtained in one pot reaction of **9a** with ethyl acrylate in refluxing CH_3CN for 20 h in 71% yield. Palladium catalyzed nucleophilic reaction using allylic sulfones has been reported.[10)] Reaction of **13** or **25** with dimethyl sodio methylacetoacetate gave **26** in 65% and 71% yields.

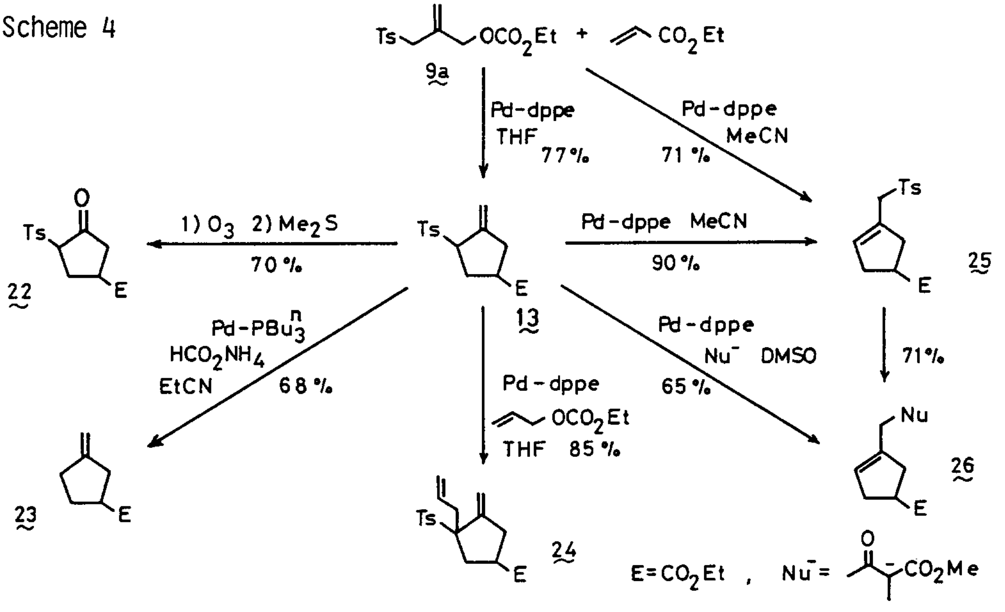
Table 1. Palladium-Catalyzed [3 + 2] Cycloadditions with **9a** and **9b**[a)]

Run	Carbonate	Olefin	Time(h)	Product[b)]		Yield(%)[c)]
1	**9a**		20		(**13**)	77
2[d)]	**9b**		2		(**14**)	66
3	**9b**		20		(**15**)	72
4	**9a**		10		(**16**)	65
5	**9b**		18		(**17**)	71
6	**9a**		1		(**19**)	89
7	**9b**		1		(**19**)	51
8	**9a**		24		(**20**)	61
9	**9b**		18		(**21**)	73

a) Reactions were carried out using **9a** or **9b** (0.5 mmol), olefin (1.0 mmol), $Pd_2(dba)_3.CHCl_3$ (0.0125 mmol), and dppe (0.05 mmol) in refluxing THF (5 mL) under argon. b) All products were identified by ^1H NMR, ^{13}C NMR, and IR analyses. c) Isolated yield after column chromatography. d) 2.5 mmol of ethyl acrylate was used.

The present method is useful for the synthesis of cyclopentanoid natural products. Further development is in progress.

Scheme 4



Reference and Note:

1. See; L. A. Paquette et al., "Recent Developments in Polycyclopentanoid Chemistry" Tetrahedron, **37**, 4359 (1981).
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