

Pd(II)-CATALYZED 1,3-ALKYL MIGRATION OF 1-ALKENYL ETHYL ACETALS.
PREPARATION OF α -ALKYLATED (E)- α,β -UNSATURATED CARBONYL COMPOUNDS

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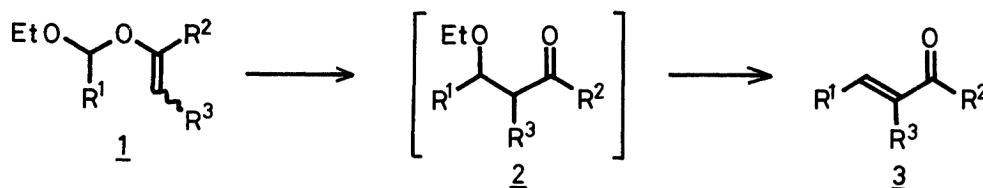
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Palladium(II) complexes, such as $(\text{CH}_3\text{CN})_2\text{PdCl}_2$ and $(\text{diene})\text{PdCl}_2$, catalyze 1,3-alkyl migration of 1-alkenyl ethyl acetals and subsequent elimination of ethanol to give α -alkylated (E)- α,β -unsaturated carbonyl compounds in excellent yields.

In the preceding papers we described the 1,3-alkyl migration of 2-alkyl-4,5-dihydro-1,3-dioxepines¹⁾ and acyclic 1-alkenyl alkyl acetals²⁾ catalyzed by boron trifluoride. We wish to report here a new method for the preparation of α -alkylated α,β -unsaturated carbonyl compounds via 1,3-alkyl migration and subsequent elimination of ethanol catalyzed by palladium(II) complexes.

1-Alkenyl ethyl acetals, 1, prepared from ethyl vinyl ether and allylic alcohols were treated with catalytic amounts of $(\text{CH}_3\text{CN})_2\text{PdCl}_2$ at room temperature for 0.5-1 h to generate quantitatively intermediary α -alkyl- β -ethoxy carbonyl compounds, 2,³⁾ from which ethanol was eliminated to afford α -alkylated (E)- α,β -unsaturated carbonyl compounds, 3, exclusively by stirring for additional 1 or 3 days at ambient temperature. Weak Lewis acidity of palladium(II) complex may permit selective elimination of ethanol from 2 without any side-reaction.⁴⁾ Selected examples of Pd(II)-catalyzed 1,3-alkyl migration and subsequent elimination of ethanol are listed in Table 1.



Experimentally, to a solution of acetaldehyde ethyl 1-propenyl acetal, 1a, (1.31 g, 10 mmol) in dichloromethane (15 ml) was added the catalytic amounts of dichlorobis(acetonitrile)palladium (0.26 g, 1.0 mmol). The reaction mixture was stirred for 30 min at room temperature. ¹H-NMR spectrum and GLC analysis disclosed the production of 3-ethoxy-2-methylbutanal, 2a, in a quantitative yield. After stirring for an additional 1 day, catalyst was removed by bulb to bulb distillation. The resulting distillate was washed with 50 ml of aqueous potassium carbonate (0.05 N), and dried over calcium chloride. Removal of solvent under reduced pressure gave 2-methyl-2-butenal, 3a, in a 71% (0.6 g) yield.

Catalytic activity was tested briefly with several palladium complexes using

Table 1. Preparation of α -Alkylated (E)- α,β -Unsaturated Carbonyl Compounds Catalyzed by $(\text{CH}_3\text{CN})_2\text{PdCl}_2$ ^{a)}

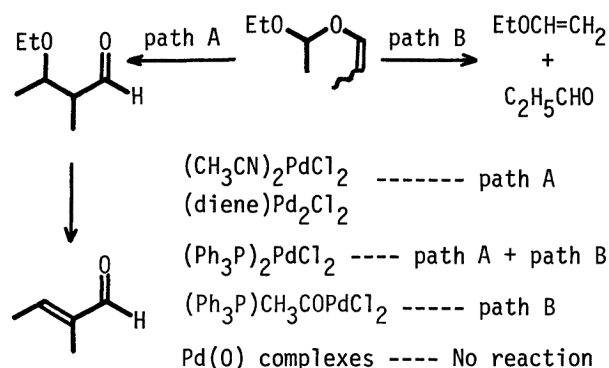
<u>1</u>	R ¹	R ²	R ³	[<u>1</u>]/[Pd(II)]	Time(h)	Yield(%) ^{b)} of <u>3</u>
a	CH ₃	H	CH ₃	10	24	71
b	CH ₃	H	CH ₃	13	36	80
c	C ₂ H ₅	H	CH ₃	5	45	82
d	C ₂ H ₅	H	C ₂ H ₅	9	43	78
e	n-C ₃ H ₇	H	CH ₃	10	35	86
f	CH ₃	CH ₃	CH ₃	9	72	84
g	CH ₃	n-C ₃ H ₇	CH ₃	10	50	85
h	CH ₃	C ₂ H ₅	C ₂ H ₅	10	50	87

a) Satisfactory spectral and analytical data were obtained for all products.

b) Isolated yield.

acetaldehyde ethyl 1-propenyl acetal as a reactant. $(\text{CH}_3\text{CN})_2\text{PdCl}_2$ and $(\text{diene})\text{PdCl}_2$ (diene=1,5-cyclooctadiene and dicyclopentadiene) effectively catalyzed the reaction to give 2-methyl-2-butenal (path A), however Pd(II) complexes having phosphorus ligands caused a side-reaction which yielded ethyl vinyl ether and propanal (path B). Pd(0) complexes, such as $(\text{Ph}_3\text{P})_4\text{Pd}$ and $(\text{dba})_3\text{Pd}_2$ (dba=dibenzylideneacetone), were also tested but these complexes failed to effect the reaction under the comparable conditions (Scheme). The reaction paths depend seriously on the bulkiness of the ligands and/or the coordination ability toward Pd(II) center. Only relatively weak ligands such as CH_3CN and dienes may permit the interaction (electrostatic attraction or coordination) of intermediary oxygen-stabilized carbo-cation with Pd(II) center to give 3 by way of an intermediate 2.

Scheme



In conclusion, variously substituted α,β -unsaturated carbonyl compounds can be prepared via selective cross (for example run d and e) and regioselective (run g and h) aldol type reactions catalyzed by Pd(II) complexes, and this reaction seems to become a useful method in organic synthesis.

References

- 1) H. Suzuki, H. Yashima, T. Hirose, M. Takahashi, Y. Moro-oka, and T. Ikawa, *Tetrahedron Lett.*, **21**, 4927 (1980).
- 2) M. Takahashi, H. Suzuki, Y. Moro-oka, and T. Ikawa, submitted to *Chem. Lett.*
- 3) Formation of intermediary α -alkyl- β -ethoxyaldehydes and ketones was confirmed by means of $^1\text{H-NMR}$ spectra and GLC analysis.
- 4) Strong Lewis acids, such as trifluoroborane etherate and aluminum trichloride, also gave α -alkyl- β -ethoxy carbonyl compounds at lower temperature (-78°C), however with a rise in temperature they gave several polycondensation products besides expected α,β -unsaturated carbonyl compounds.

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