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PALLADIUM-CATALYZED REARRANGEMENT OF ALLYLIC ESTERS OF ACETOACETIC ACID TO GIVE γ,δ-UNSATURATED METHYL KETONES

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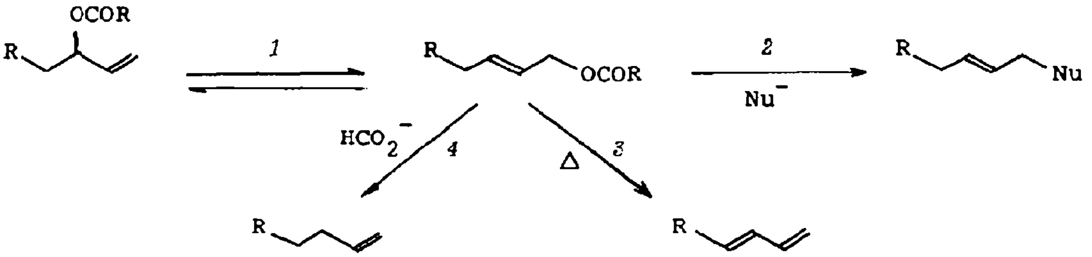
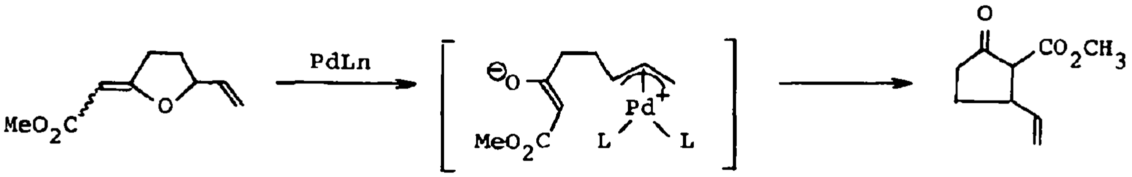
Summary: Various allylic esters of acetoacetic acid undergo rearrangement to give γ,δ-unsaturated methyl ketones in high yields with elimination of carbon dioxide under mild conditions in the presence of catalytic amounts of $Pd(OAc)_2$ and PPh_3.

It is known that allylic esters undergo four reactions catalyzed by palladium compounds. *1*. Allylic rearrangement,1) *2*. displacement with nucleophiles2) *3*. elimination to give conjugated dienes,3) and *4*. hydrogenolysis to give monoenes.4)



In our continuous studies on the palladium-catalyzed reactions of various allylic compounds, we have reported the Claisen rearrangement of the allyl vinyl ether 1 to 2-methoxycarbonyl-3-vinylcyclopentanone (3) by intramolecular attack of the carbanion of β-keto ester on the intermediate π-allylpalladium complex 2.5)



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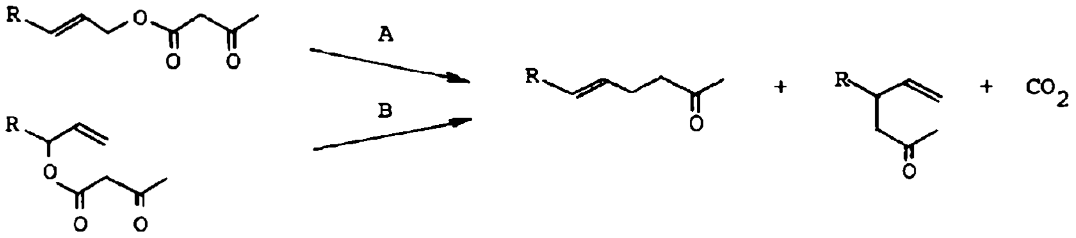
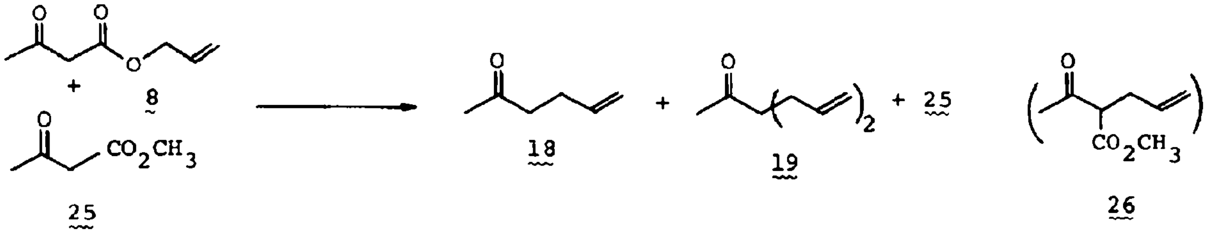
In this paper, we wish to report that allylic esters of acetoacetic acid undergo the palladium-catalyzed rearrangement to give γ,δ-unsaturated methyl ketones with elimination of carbon dioxide as expressed by the following general scheme.



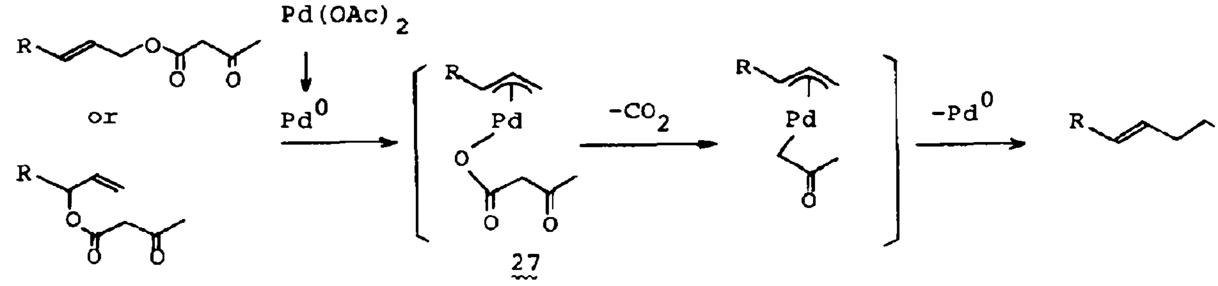
The reaction route B in the scheme is called the Carroll rearrangement, which proceeds thermally above 170°C.[7,8] The palladium-catalyzed reaction, we have discovered, proceeds in refluxing THF, or at lower temperature by using catalytic amounts of Pd(OAc)$_2$ and PPh$_3$ to give the rearranged products in high yields.

In a typical example, (*E*)-1-methyl-2-butenyl acetoacetate (**4**) (2 mmol) was refluxed in THF (20 ml) in the presence of Pd(OAc)$_2$ (0.1 mmol) and PPh$_3$ (0.4 mmol) and (*E*)-4-methyl-5-hepten-2-one (**5**) was obtained in nearly quantitative yield with retention of *E* form of the double bond. Results of the reactions of various allylic esters of acetoacetic acid are summarized in the Table. Diallylated compounds were obtained together with monoallylated products in the reactions of **6**, **7**, and **8**. When the reaction of allyl acetoacetate (**8**) was carried out in the presence of methyl acetoacetate (**25**), 2-allylated acetoacetate (**26**) was not formed However, in this reaction diallylacetone (**19**) was a major product and allylacetone (**18**) was a minor product.

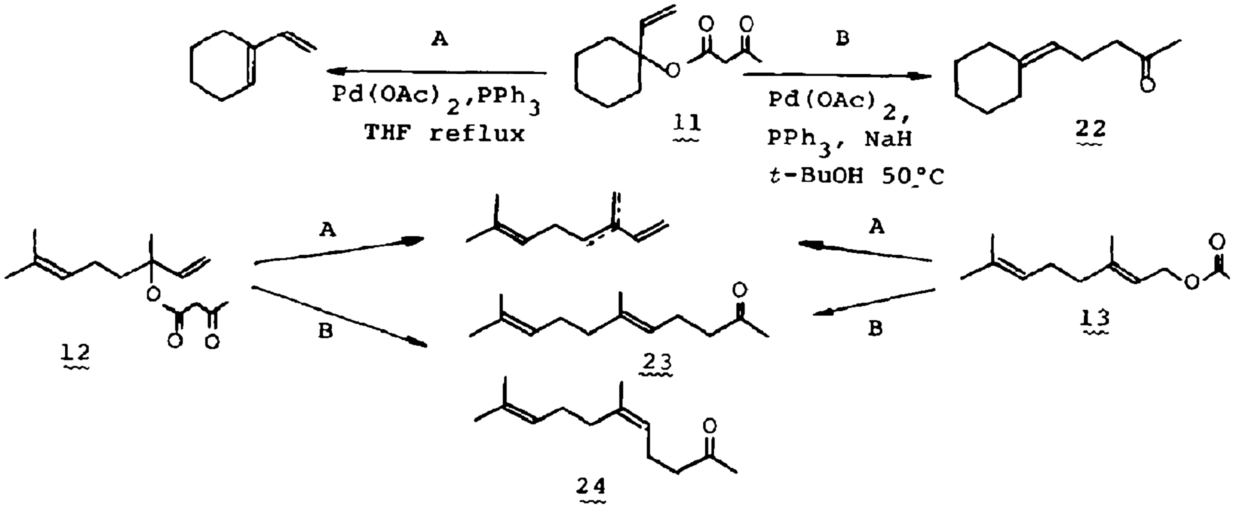


In the reactions of **6**, **11**, **12**, and **13** the acetonyl group was introduced exclusively at the terminal position. However, two monoallylated products **16** and **17** were obtained in a ratio of 3 : 1 from 2,7-octadienyl acetoacetate (**7**). Reaction of 2,2-disubstituted acetoacetates **9** and **10** gave the α-trisubstituted ketones by regioselective displacement of the allyl ester groups without attacking unsubstituted side. This is an efficient preparative method for trisubstituted methyl ketones. Thermal Carroll rearrangement which is believed to proceed through enolization to form a 1,5-diene is impossible with these compounds.

This reaction can be explained by the following mechanism. The first step is the oxidative addition of allylic esters to Pd^0 species formed from Pd(OAc)$_2$ and PPh$_3$ to form the π-allyl palladium complex **27**, coordinated by acetoacetate anion, which undergoes decarboxylation. Similar facile decarboxylation was observed with coordinated formate anion to form palladium hydride species in the palladium catalyzed hydrogenolysis of allylic esters.[4] Then the nucleophili attack of the coordinated carbanion of acetone mainly to less substituted sid the π-allylic system gives the product.

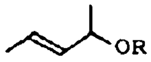
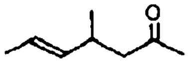
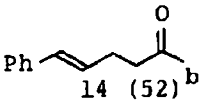
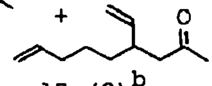
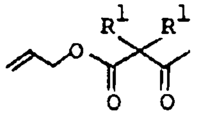
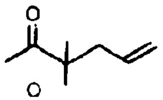
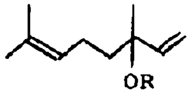
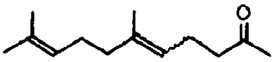
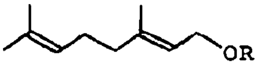
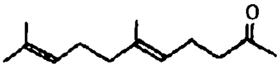


Reactions of esters of tertiary allyl alcohols such as 11, 12, and 13 wi Pd(OAc)$_2$-PPh$_3$ in refluxing THF gave the dienes as the elimination products pr inantly.[3] But reaction of 11 (2 mmol) in the presence of NaH (2 mmol), Pd(O (0.1 mmol) and PPh$_3$ (0.4 mmol) in *t*-BuOH (20 ml) at 50°C for 1 h gave the γ,δ- unsaturated ketone 22 without elimination in 51% yield after chromatographic purification. Under the same conditions linalyl acetoacetate (12) gave geran acetone (23) and nerylacetone (24) in a ratio of 3 : 2, but geranyl acetoacet (13) was converted to geranylacetone (23) with retention of *E* form of the dou bond. These results were well understood by the fact that the π-allylic pall intermediate formed kinetically from 13 was syn only whereas that from 12 was mixture of syn and anti forms.[9]



Since all allylic esters of acetoacetic acid reported in this paper were easily prepared from corresponding allylic alcohols and diketene,[8] this reac offers a convenient synthetic method for γ,δ-unsaturated methyl ketones from allylic alcohols. Further extention of this reaction is in progress.

Table. Reactions of Allylic Esters of Acetoacetic Acid with $Pd(OAc)_2$-PPh_3

R = $COCH_2COCH_3$	Method[a)]	Reaction Time	Products (Yield, %)
4 	A	1 h	 5 (100)^c
6 	A	1 h	 14 (52)^b  15 (21)^b
7 	A	20 min	 16 (24)^b +  17 (8)^b + d
 8 R^1=H	A	30 min	18 + 19 (100)^c (18 : 19 = 2 : 3)^c
9 R^1=CH_3	A	1 h	 20 (100)^c
10 R^1= 	A	2 h	 21 (93)^b
 12	B	2 h	 23 + 24 (56) E : Z = 3 :
 13	B	4 h	 23 (44)^b

a) Method A. Allylic ester (2 mmol), $Pd(OAc)_2$ (0.1 mmol), PPh_3 (0.4 mmol) in refluxing THF (20 ml). Method B. Allylic ester (2 mmol), NaH (2 mmol), $Pd(OAc)_2$ (0.1 mmol), PPh_3 (0.4 mmol) in *t*-BuOH (20 ml) at 50°C. b) Isolated yield by column chromatography. c) GLC analysis. d) Diallylated products (32%)^b.

References:
1)a) J.Tsuji, K.Tsuruoka, K.Yamamoto, Bull. Chem. Soc. Jpn., 49, 1701 (1976); b) L.E.Overman, F.M.Knoll, Tetrahedron Lett., 1979, 321. 2)a) K.Takahashi, A.Miyake, G.Hata, Bull. Chem. Soc. Jpn., 45, 230 (1972); b) K.E.Atkins, W.E.Walker, R.M. Manyik, Tetrahedron Lett., 1970, 3821. 3) J.Tsuji, T.Yamakawa, M.Kaito, T.Mandai, Tetrahedron Lett., 1978, 2075. 4) J.Tsuji, T.Yamakawa, Tetrahedron Lett., 1979, 613. 5) J.Tsuji, H.Kataoka, Y.Kobayashi, T.Takahashi, Tetrahedron Lett., in press. 6) Recently a similar reaction catalyzed by $Pd(PPh_3)_4$ in DMF has been reported, T.Tsuda, Y. Chujo, K.Tawara, T.Saegusa, Abst. 41th Ann. Meeting Japan Chem. Soc., II, 859 (1980). 7) M.F.Carroll, J. Chem. Soc., 1940, 704, 1266, and 1941, 507. 8) W.Kimel, A.C.Cope, J. Am. Chem. Soc., 65, 1992 (1943). 9) B.M. Trost, T.M.Verhoeven, J. Org. Chem., 41, 3215 (1976).

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