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PALLADIUM-CATALYZED ALLYLATION OF KETONES AND ALDEHYDES VIA ALLYL ENOL CARBONATES

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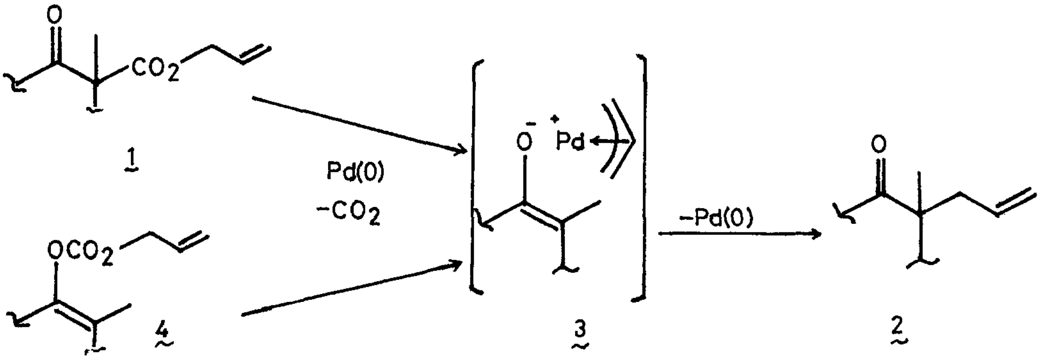
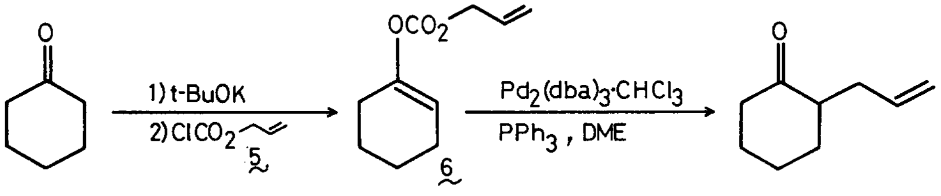
Summary: Rearrangement of allyl enol carbonates, prepared from ketones or aldehydes by trapping their enolates with allyl chloroformate, to give α-allyl ketones or aldehydes regioselectively is catalyzed by palladium-phosphine complexes under mild condtions.

Palladium catalyzed allylation is a useful synthetic method.[1,2] The allylation takes place most smoothly with active methylene compounds such as malonates, β-keto esters, and β-diketones, but the direct allylation of simple ketones is difficult to carry out under usual conditions. So far three reports have been given on the allylation of ketones via their lithium,[3] tin,[4] and boron[5] enolates

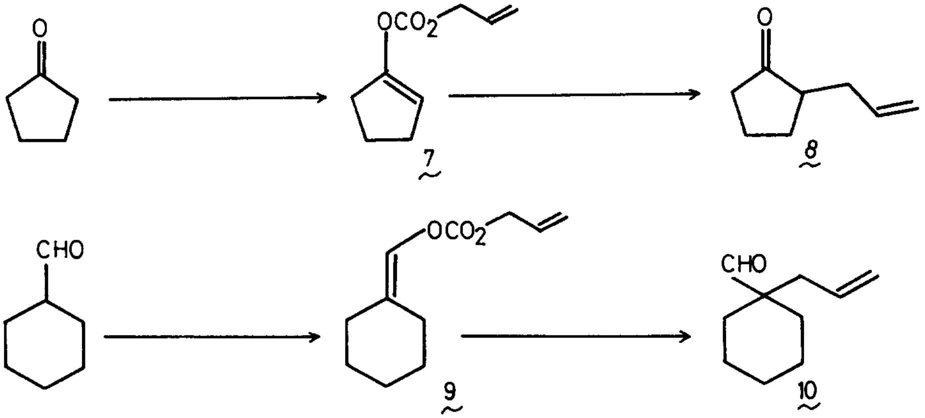
In the previous paper, we have reported the palladium catalyzed very smooth rearrangement of allyl esters of β-keto acids 1 to give α-allyl ketones 2 (palladium catalyzed Carroll rearrangement).[6,7] The rearrangement can be explained by the formation of the π-allylpalladium enolate 3 as a key intermediate by the oxidative addition and decarboxylation. Finally the α-allyl ketone is formed by reductive coupling. Furthermore, we found that allyl carbonates are extremely good allylating agents of active methylene compounds.[8] Allyl carbonates are much more reactive than commonly used allyl acetates, and the allylation with carbonates proceeds under mild and neutral conditions. But poor results were obtained by the reaction of simple ketones with allyl carbonates. Based on these results, we expected that the same palladium enolate complexes 3 is formed from allyl enol carbonates 4. In this communication, we wish to report the palladium catalyzed regioselective allylation of simple ketones via allyl enol carbonates.



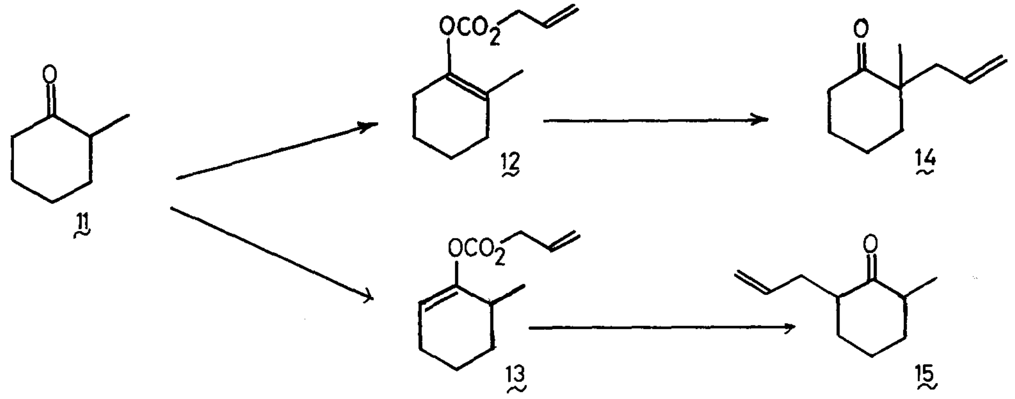
In a typical example, allyl 1-cyclohexenyl carbonate (6)9) (1 mmol) was added to a DME (5 mL) solution of $Pd_2(dba)_3 \cdot CHCl_3$10) (0.1 mmol) and PPh_3 (0.4 mmol) at 0°C. The mixture was stirred at 0°C under argon for 30 min, and 2-allylcyclohexanone was obtained in 91% yield after chromatographic purification (silica gel/ether-hexane).



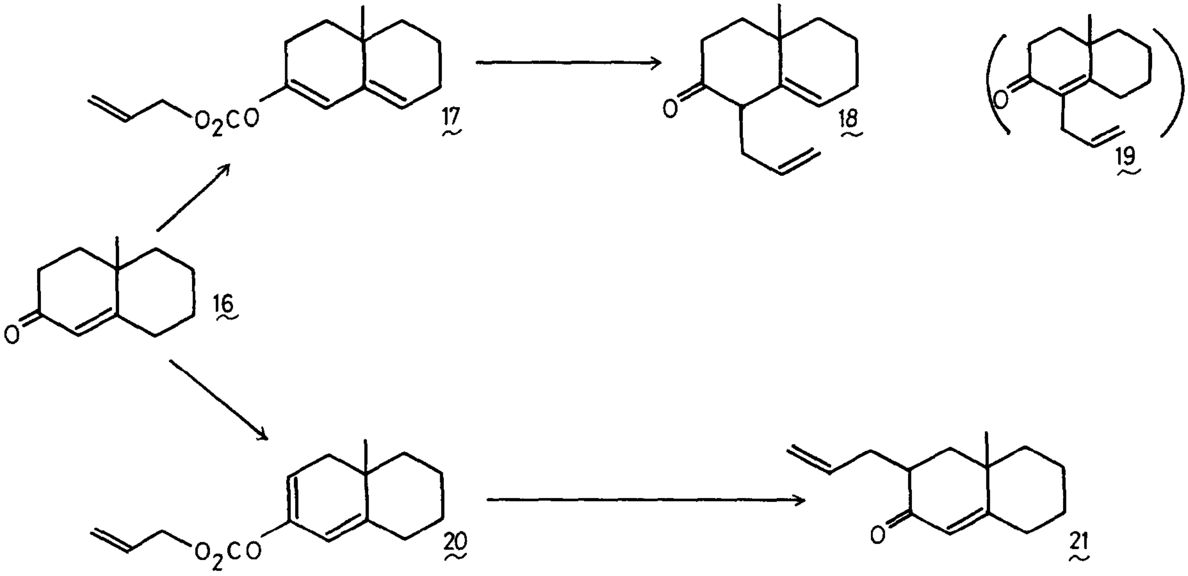
Allyl enol carbonates 7 and 9, prepared from cyclopentanone and cyclohexanecarbaldehyde, were converted similarly to 2-allylcyclopentanone (8) (82%) and α-allylated aldehyde 10 (64%).



High regioselectivity was confirmed by the reaction of 2-methylcyclohexanone (11). The enol carbonate 12 was prepared by quenching the thermodynamically stable potassium enolate of 11 at 25°C with allyl chloroformate (5) as a 93/7 mixture of 12 and 13 (by HPLC). The reaction of 12 thus prepared without separation of 13, gave a mixture of 2-allyl-2-methylcyclohexanone (14) and 6-methyl-2-allylcyclohexanone (15) (14/15 = 95/5 by HPLC) in 82% yield. On the other hand, the less substituted enol carbonate 13, prepared from kinetically generated potassium enolate of 11 at 0°C (99/1 mixture of 13/12), was converted to 15 and 14 (15/14 = 98/2 by HPLC) in 83% yield. These results clearly show that the palladium catalyzed allylation of cyclohexanone via the enol carbonates proceeds regioselectively.



Regioselective monoallylation of the 10-methyl-$\Delta^{1,9}$-2-octalone (16) was also carried out via its enol carbonates. The dienyl carbonate 17 was prepared from the thermodynamically stable potassium enolate of 16 (*t*-BuOK in DMF at room temperature in 68% yield). The palladium-catalyzed reaction of 17 gave the 1-allylated octalone 18 as a sole product in 78% yield. IR and NMR spectra showed the olefin was deconjugated.[11] No isomerization of the allylated product 18 to the more stable conjugated enone 19 took place since this reaction proceeded under neutral conditions. The other dienyl carbonate 20, prepared from kinetically generated enolate of 16 [KN(SiMe$_3$)$_2$ in THF at -70°C in 50% yield], was converted to the 3-allylated octalone 21 in 80% yield.



Regioselective alkylation of unsymmetrical ketones via specifically generated enol derivatives is a current interest in organic synthesis.[12] Allylation method described here provides a new method in this field. Further application of this reaction is in progress.

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References and Notes:

1) J. Tsuji, Organic Synthesis with Palladium Compounds, Springer Verlag, 1980, Heidelberg.
2) a) B. M. Trost, Tetrahedron, 33, 2615 (1977).
b) B. M. Trost, Acc. Chem. Res., 13, 385 (1980).
3) M. C. Fiaud, J. L. Malleron, Chem. Commun., 1981, 1159.
4) B. M. Trost, E. Keinan, Tetrahedron Lett., 21, 2591 (1980).
5) E. Negishi, H. Matsushita, S. Chatterjee, R. A. Joh, J. Org. Chem., 47, 3188 (1982).
6) I. Shimizu, T. Yamada, J. Tsuji, Tetrahedron Lett., 21, 3199 (1980).
7) T. Tsuda, Y. Chujo, S. Nishi, K. Tawara, T. Saegusa, J. Am. Chem. Soc., 102, 6348 (1980).
8) J. Tsuji, I. Shimizu, I. Minami, Y. Ohashi, Tetrahedron Lett., 23, 4809 (1982)
9) Enol carbonates 6, 7, and 9 were prepared by quenching the corresponding potassium enolates with allyl chloroformate (5). Selectivity of *O*-carboxylation of cyclohexanone to 6 increased in the order of Li < Na < K enolates.
10) T. Ukai, H. Kawazura, Y. Ishii, J. Organomet. Chem., 65, 253 (1974).
11) IR and NMR spectral data for 12, 13, 17, 18, 20, and 21 are as follows: 12 NMR (CCl_4, δ) 1.40 (s, 3H, CH_3), 4.52 (d, J = 5 Hz, 2H, $-OCH_2-$), 5.00-6.30 (m, 3H, $CH=CH_2$); IR (neat) 1760 cm^{-1}: 13 NMR (CCl_4, δ) 0.95 (d, J = 7 Hz, 3H, CH_3), 4.52 (d, J = 5 Hz, 2H, $-OCH_2-$), 5.0-6.2 (m, 4H, $CH=CH_2$ and $-CH=CH$); IR (neat) 1760, 1650 cm^{-1}: 17 NMR (CCl_4, δ) 1.0 (s, 3H, CH_3), 4.52 (d, J = 5 Hz, 2H, $-OCH_2=$) 5.0-6.3 (m, 5H, $CH=CH_2$ and $=CH-C=CH$); IR (neat) 1760, 1670, 1640 cm^{-1}: 18 NMR (CCl_4, δ) 1.3 (s, 3H, CH_3), 2.9-3.3 (m, 1H, $CO-\overset{|}{C}\underline{H}-C=C$), 4.8-6.3 (m, 4H, $CH=CH_2$ and $-C=CH-$); IR (neat) 1720, 1640 cm^{-1}: 20 NMR (CCl_4, δ) 1.0 (s, 3H, CH_3), 4.55 (d, J = 5 Hz, $-OCH_2-$), 5.08-6.03 (m, 5H, $-HC=C-CH=$ and $CH=CH_2$); IR (neat) 1760, 1670 cm^{-1}: 21 NMR (CCl_4, δ), 1.22 (s, 3H, CH_3), 4.70-6.10 (m, 3H, $CH=CH_2$), 5.58 (bs, 1H, $COCH=$); IR (neat) 1670, 910 cm^{-1}.
12) J. d'Angelo, Tetrahedron, 32, 2979 (1976).

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