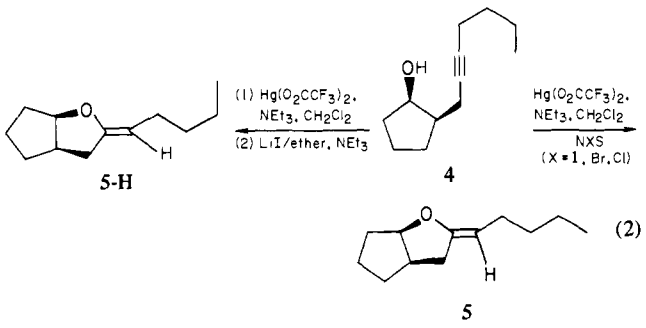
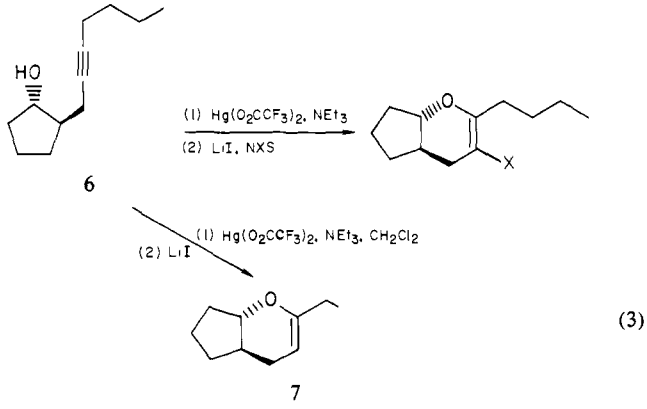


After an additional 3 h, 0.1 mL (0.72 mmol) of NEt_3 was added. Workup and separation by LC (SiO_2, ether/hexanes (15:85, +4% NEt_3)) gave product **5**-H[12] (21 mg, 0.12 mmol, 45%, purity by GC = 99%) and recovered starting material (24 mg, 0.13 mmol, 50%). At −78 °C 0.05 mL (0.25 mmol) of cis-acetylenic alcohol **4** was added to a solution of 110 mg (0.25 mmol) of $Hg(O_2CCF_3)_2$, 0.038 mL (0.27 mmol) of NEt_3, and 58 mg (0.26 mmol) of NIS. The reaction was stopped after 15 min by addition of 0.2 mL (1.44 mmol) of NEt_3 and warming to room temperature. Concentration and separation by LC (SiO_2, ether/hexanes (15:85, +4% NEt_3)) yielded 67 mg (0.22 mmol, (87%) of cis-iodoenol ether **5** (X = I).[13] Similar procedures gave the β-bromo- (88%)[14,15] or β-chloroenol (32%)[16] ethers. The β-halo compounds were subjected to hydrolysis conditions more vigorous than physiological ones: as the electron-withdrawing ability of the halogen substituent increased, stability toward hydrolysis also *increased* (see Table I).

Mercury-induced cyclization of the trans isomer occurred at a rate slower than that noted for the cis isomer and gave the thermodynamically favored endocyclic product (**7**, eq 3) directly



(86% after chromatograhy on silica, based on **6**).[17,18] Here, the intermediary organomercury compound could by isolated.[19] The iodo-, bromo-, and chloroenol ethers were obtained in 88%, 76%, and 82% yields, respectively, based on **6**, after chromatography on silica) and were subjected to hydrolysis conditions (see Table I).

It may be for the prostacyclin series, as in the model cases noted above, in which a cis fusion of the bicyclic enol ether moiety is a requirement, that formation of the 5,5-bicyclic species is *kinetically* preferred. In the corresponding trans-fused case such a ring system may not be feasible on strain grounds, and therefore, only slower cyclization to give the 5,6-endocyclic species can occur. General rules for acetylenic alcohol cyclization remain to be elucidated.

Acknowledgment. We acknowledge support for this work provided by the National Institutes of Health (Grant No. HL22612).

Registry No. 1, 83096-84-8; **2**, 83096-85-9; **2**-endo, 83096-95-1; **3**, 83114-94-7; **4**, 83096-86-0; **5**-H, 83096-87-1; **5** (X = I), 83096-88-2; **5** (X = Br), 83096-89-3; **5** (X = Cl), 83096-90-6; **6**, 83096-91-7; **7**, 83096-92-8; $HgCl_2$, 7487-94-7; $Hg(O_2CCF_3)_2$, 13257-51-7; *trans* 2-butyl-3-iodo-4,4a,5,6,7,7a-hexahydrocyclopenta[*b*]pyran, 83114-95-8; *trans*-3-bromo-2-butyl-4,4a,5,6,7,7a-hexahydrocyclopenta[*b*]pyran, 83096-93-9; *trans*-2-butyl-3-chloro-4,4a,5,6,7,7a-hexahydrocyclopenta-[*b*]pyran, 83096-94-0.

(12) ^1H NMR (C_6D_6) δ 4.96 (t × t, J = 7.2 × 1.8 Hz), 4.49 (m, 1), 2.6–1.1 (m, 15), 0.93 (t, 3, J = 6.3 Hz). Exact mass: calcd, 180.1514; found, 180.1522 ± 0.0018.

(13) ^1H NMR (C_6D_6) δ 4.52 (m, 1), 2.8–1.0 (m, 15), 0.90 (t, 3, J = 6.4 Hz); $^{13}C\{^1H\}$ δ 155.6, 81.5, 68.1, 43.3, 42.6, 37.9, 29.7, 28.7, 27.1, 22.6, 20.0, 14.1. Exact mass: calcd, 306.0482; found, 306.0454 ± 0.003.

(14) ^1H NMR (C_6D_6) δ 4.51 (m, 1), 2.8–1.0 (m, 15), 0.90 (t, 3, J = 6.4 Hz); $^{13}C\{^1H\}$ δ 155.0, 97.9, 90.1, 41.2, 38.7, 34.5, 33.6, 33.3, 30.7, 24.2, 21.9, 14.0. Exact mass: calcd, 258.0620; found, 258.0603 ± 0.0025.

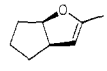
(15) In the absence of mercuric salts, the reaction between **4** and NBS gave only polybrominated products, as did treatment of **4** simultaneously with Hg(II) and NBS.

(16) The chloro compound could not be purified satisfactorily by chromatography. The ^1H NMR spectrum was similar to that of the β-bromo analogue. Exact mass: calcd, 214.1124; found, 214.1106 ± 0.002.

(17) **7**: ^1H NMR (C_6D_6) δ 4.52 (m, 1), 3.46 (m, 1), 2.24–1.14 (m, 15), 0.89 (t, 3, J = 6.4 Hz); $^{13}C\{^1H\}$ δ 156.0, 95.3, 81.7, 39.9, 34.3, 29.9, 29.0, 28.3, 27.8, 22.6, 19.9, 14.1. Exact mass: calcd, 180.1514; found, 180.1514 ± 0.0018.

(18) Cyclization to **7** could be effected successfully by using a catalytic amount of Hg(II) salts either in the presence (slowly) or absence (rapidly) of base or with $Pd(OAc)_2$ in CH_2Cl_2 (slowly).

(19) In the presence of 2 equiv of NEt_3, the di(alkenyl)mercury derivative **9** could be isolated (15%, after chromatography on silica): ^1H NMR (C_6D_6) δ 3.26 (m, 1), 2.0–1.0 (m, 15), 0.85 (t, 3, J = 6 Hz). This species could be converted to the corresponding β-halogen enol ethers in high yield.



2-endo

Palladium-Catalyzed Decarboxylation–Dehydrogenation of Allyl β-Keto Carboxylates and Allyl Enol Carbonates as a Novel Synthetic Method for α-Substituted α,β-Unsaturated Ketones

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Received May 26, 1982

β-Keto esters are important intermediates for selective alkylation of ketones. Usually after the alkylation, the ester group as the activating group of the ketone is removed by hydrolysis and subsequent decarboxylation. If the ester group is removed oxidatively, instead of by simple decarboxylation, such a method would be very useful for further transformation. In this communication, we report the facile formation of α,β-unsaturated ketones from β-keto esters under very mild conditions.

In a previous paper, we have reported the palladium-catalyzed rearrangement of allylic esters of acetoacetic acid to form γ,δ-unsaturated methyl ketones (the Pd-catalyzed Carroll rearrangement).[1,2] In the course of further studies on this reaction with cyclohexanone derivatives, we found a profound effect of the ligand: the decarboxylation–dehydrogenation took place to give 2-alkyl-2-cyclohexenones (**2**, Scheme I) from allyl 2-alkylcyclohexanone-2-carboxylates (**1**) by using 1,2-bis(diphenylphosphino)ethane (dppe), instead of PPh_3, as the ligand. In a typical example, allyl 2-methylcyclohexanone-2-carboxylate (**1a**) (1 mmol) in CH_3CN was refluxed for 30 min in the presence of

(1) Shimizu, I.; Yamada, T.; Tsuji, J. *Tetrahedron Lett.* **1980**, *21*, 3199–3202.

(2) Tsuda, T.; Chujo, Y.; Nishi, S.; Tawara, K.; Saegusa, T. *J. Am. Chem. Soc.* **1980**, *102*, 6381–6384.

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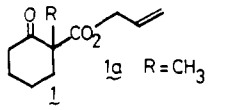
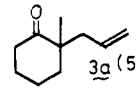
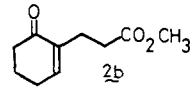
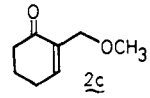
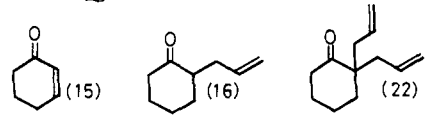
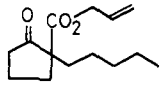
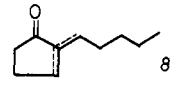
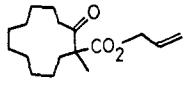
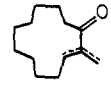
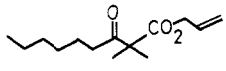
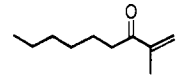
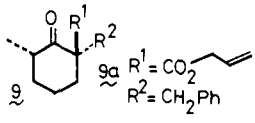
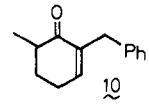
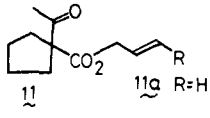
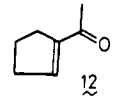
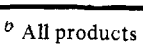
Table I. Reaction of Allyl β-Ketocarboxylates with Pd–dppe Catalyst[a]

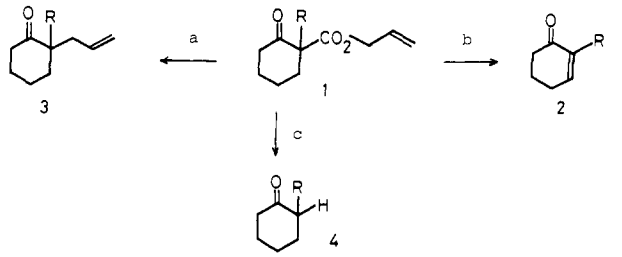
Entry	Ester	Solvent	Reaction Time (min)	Products[b], Yield%[c]
1	 1a R=CH$_3$	CH$_3$CN	30	 2a(85)  3a(5)
2	1a	DMF[d]	30	2a(79) 3a(6)
3	1a	CH$_3$COCH$_3$	30	2a(3) 3a(86)
4	1a	t-BuOH	30	2a(1) 3a(76)
5	1b R=CH$_2$CH$_2$CO$_2$CH$_3$	CH$_3$CN	60	 2b 82
6	1c R=CH$_2$OCH$_3$	CH$_3$CN	30	 2c (46)
7	1d R=H	CH$_3$CN	20	 (15) (16) (22)
8		CH$_3$CN	40	 81(endo:exo 4:1)
9		CH$_3$CN	60	 79(endo:exo 5:3)
10		CH$_3$CN	30	 76
11	 9 9a R^1=CO$_2$ R^2=CH$_2$Ph	CH$_3$CN	40	 10 80
12	9b R^1=CH$_2$Ph R^2=CO$_2$	CH$_3$CN	40	10 89
13	 11 11a R=H	dioxane	15	 12 (57)
14	11b R=Ph	dioxane	30	12 (82) +  (81)

[a] Reactions were carried out with 2–10 mol % of Pd(OAc)$_2$ and dppe in boiling solvents under nitrogen. [b] All products were identified by NMR and IR spectra. [c] Isolated yield. GLC yield in parenthesis. [d] 100 °C.

Pd(OAc)$_2$ (0.05 mmol) and dppe (0.05 mmol). GLC analysis showed the formation of 2-methyl-2-cyclohexenone (**2a**) in 85% yield with a small amount of 2-methyl-2-allylcyclohexanone (**3a**).

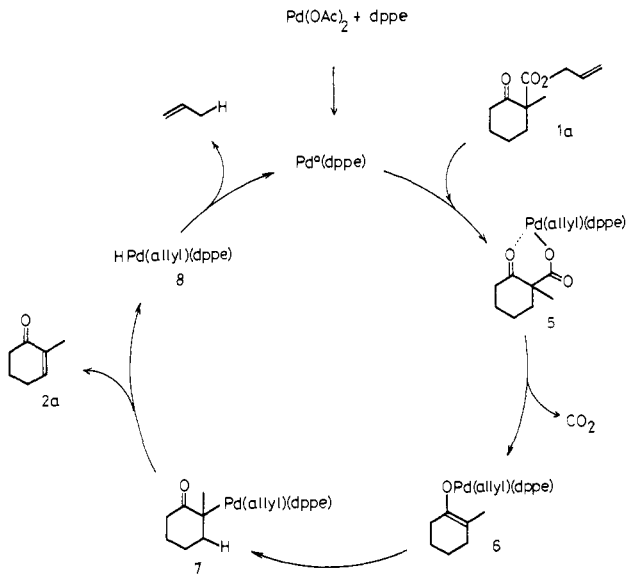
Results of experiments under different conditions with several substrates are shown in Table I. In this reaction, the choice of solvent is important (entries 1–4). Aprotic solvents such as CH$_3$CN and DMF were the best for the enone formation. On the other hand, in acetone and *tert*-butyl alcohol, the allylated products **3** were the main products even when dppe was used. In addition, the presence of a substituent at the α position is essential for the selective enone formation. For example, the reaction of allyl cyclohexanone-2-carboxylate (**1d**) was not selective and produced a mixture of cyclohexenone and 2-allyl- and 2,2-diallylcyclohexanones with the Pd–dppe catalyst (entry 7). Only endocyclic olefins were obtained from cyclohexanones **1a–c** and **9**, but exo double-bonded cyclic ketones were obtained as minor

Scheme I[a]



[a] Key: (a) Pd-PPh_3; (b) Pd-dppe in CH_3CN; (c) $PdCl_2(PPh_3)_2$, HCO_2NH_4 in dioxane.

Scheme II



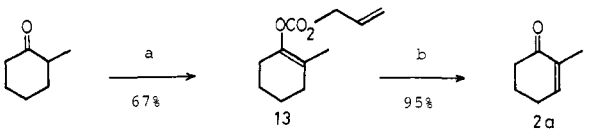
products from allyl 2-pentylcyclopentanone-2-carboxylate and allyl 2-methylcyclododecanone-2-carboxylate (entries 8 and 9). The regioselective introduction of the olefin was fully confirmed by the reaction of 2,6-dialkylated cyclohexanone derivative (entries 11 and 12).

The main product of the reaction of **1** was **3** when the Pd-PPh_3 catalyst was used. Furthermore, **1a** was converted to 2-methylcyclohexanone (**4**, R = CH_3) in 87% yield by decarboxylation in boiling dioxane in the presence of ammonium formate by using $PdCl_2(PPh_3)_2$ as the catalyst.[3] Thus the above shown three useful Pd-catalyzed transformations are possible under different conditions, and they enhance the usefulness of the β-keto esters. Particularly the facile enone formation has high synthetic value, which is difficult to achieve by other means.[4]

The enone formation is explained by the following mechanism (Scheme II). The oxidative addition of the allyl ester **1a** to Pd(0) species, formed in situ from $Pd(OAc)_2$, affords allylpalladium β-keto carboxylate **5**,[5] which undergoes decarboxylation to produce the allylpalladium enolate complex **6**, which is in equilibrium with the carbon-bonded complex **7**. Then the enone **2a** is formed by the elimination of Pd-H from **7**. Finally the reductive elimination of the allylpalladium hydride complex **8** produces propene and regenerates the Pd(0) species. This reductive elimination step was confirmed by the fact that a 1:1 mixture of enone **12** and 1-phenylpropene was obtained from the cinnamyl ester of α,α-cyclopentanoacetoacetic acid (**11b**, entry 14).

The enone **2a** was also obtained by the palladium-catalyzed reaction of allyl enol carbonate **13** (Scheme III). The formation

Scheme III[a]



[a] Key: (a) *t*-AmONa in DME at 25 °C, and $ClCO_2CH_2CH{=}CH_2$ (excess); (b) $Pd(OAc)_2$-dppe (5 mol %) in CH_3CN reflux for 30 min.

of enone **2a** from **1a** and **13** strongly implies that both reactions proceed via the allylpalladium enolate **6** as the common intermediate.

Concerning the effect of the ligand on the course of the reaction, Yamamoto et al. reported that the thermal decomposition of *cis*-$PdEt_2(PMe_2Ph)_2$ gave butane by reductive coupling, and ethane and ethylene were obtained from *cis*-$PdEt_2$(dppe) by reductive elimination.[6] In this case, dppe induces the elimination to form olefin.

The conversion of ketones to α,β-unsaturated ketones by using Pd(II) salts directly[7,8] or via silyl enol ethers[9] and β-keto carboxylates[2] has been reported. But these reactions when carried out catalytically require the use of a cocatalyst to reoxidize the Pd(0).

Registry No. 1a, 7770-41-4; **1b**, 83135-28-8; **1c**, 83135-29-9; **1d**, 5453-93-0; **2a**, 1121-18-2; **2b**, 51577-39-0; **2c**, 83135-30-1; **3a**, 16178-87-3; **9a**, 83135-31-3; **9b**, 83135-32-4; **10**, 1208-44-2; **11a**, 83135-33-5; **11b**, 83135-34-6; **12**, 16112-10-0; $Pd(OAc)_2$, 3375-31-3; dppe, 1663-45-2; 2-(allyloxycarbonyl)-2-pentylcyclopentanone, 83135-35-7; 2-(allyloxycarbonyl)-2-methylcyclododecane, 83135-36-8; allyl 2-methyl-2-heptanylpropanoate, 83135-37-9; 2-cyclohexenone, 930-68-7; 2-allyl-2-cyclohexenone, 38019-50-0; 2,2-diallylcyclohexanone, 5277-36-1; 2-pentyl-2-cyclopentenone, 25564-22-1; 2-methyl-2-cyclododecenone, 83135-38-0; 2-methylene-3-monanone, 51756-19-5; 2-pentylidenecyclopentanone, 16424-35-4; 2-methylenecyclododecanone, 3045-76-9.

(3) Tsuji, J.; Yamakawa, T. *Tetrahedron Lett.* **1979**, 613-616.
(4) For the oxidative decarboxylation of carboxylic acid to form olefin with $Pb(OAc)_4$, see: Scheldon, R. A.; Kochi, J. K., *Org. React.* **1972**, *19*, 279-421.
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(6) Ozawa, F.; Ito, T.; Nakamura, Y.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1868-1880.
(7) Theissen, R. J. *J. Org. Chem.* **1971**, *36*, 752-757.
(8) Bierling, B.; Kirschke, K.; Oberender, H. *J. Pract. Chem.* **1972**, *314*, 170-180.
(9) Ito, Y.; Hirao, T.; Saegusa, T. *J. Org. Chem.* **1978**, *43*, 1011-1013.

Chiroptical Properties of *trans*-Dichlorotetrakis(pyridine)cobalt(III) Ion. A Fixed Propeller Conformation

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Received June 14, 1982

Although extensive investigations have been carried out on the stereochemical studies of coordination compounds, few reports have been found on the chiral complexes having a restricted rotation.[1] This communication describes the possible existence of a chiral metal complex with a fixed propeller conformation.

trans-Dichlorotetrakis(pyridine)cobalt(III) ion has neither configurational chirality nor conformational chirality due to a chelate ring. However, because of the steric interaction between the 2,6-hydrogens of adjacent pyridine molecules, all four pyridine rings are expected to be obliquely inclined with respect to the CoN_4 plane. This produces the torsional isomerism about the metal-

(1) (a) Nakano, Y.; Seki, H. *Chem. Lett.* **1976**, 611. (b) Nakano, Y.; Sato, S. *Inorg. Chem.* **1980**, *19*, 3391. (c) Nakano, Y.; Sato, S. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 1683.

0002-7863/82/1504-5846$01.25/0