CHEMISTRY LETTERS, pp. 1521-1522, 1980.

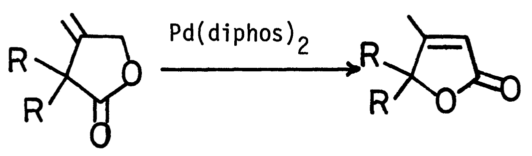
TRANSPOSITION OF CO_2 GROUP IN 2-FURANONES CATALYZED BY PALLADIUM(0)

Yoshio INOUE, Takuo HIBI, Yasuhiko KAWASHIMA, and
Harukichi HASHIMOTO
Department of Applied Chemistry, Faculty of Engineering,
Tohoku University, Sendai Miyagi 980

3,3-Dialkyl-4-methylenedihydro-2(5H)-furanone 1 isomerized into another furanone, 4-methyl-5,5-dialkyl-2(5H)-furanone 2, with transpositin of the CO_2 group in the presence of a catalytic amount of Pd(diphos)$_2$ [diphos=$Ph_2PCH_2CH_2PPh_2$].

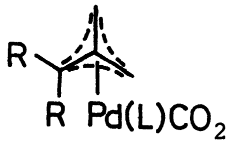
It is known that π-allyl palladium complexes are available from allylic acetate with cleavage of the C-O bond.$^{1)}$

We have found that rather unique reaction occurs with cleavage of both the C-C and the C-O bonds when a furanone bearing a suitable allylic group is treated with palladium(0): The furanone of the type 1 was converted into another furanone of the type 2 with transposition of CO_2 group in the presence of Pd(diphos)$_2$.



1 2

R , R
a -$(CH_2)_5$-
b CH_3, CH_3



L; diphos

3

The furanone of the type 2 are probably derived from the corresponding 4-methylene-furanones by isomerization.

When 3-spiro-1'-cyclohexane-4-methylenedihydro-2(5H)-furanone(1a)$^{2)}$ (0.17 mmol) was treated with an equimolar amount of Pd(diphos)$_2$ in benzene(10 ml) under CO_2 pressure(60 atm) at 125 °C for 21 h, 4-methyl-5-spiro-1'-cyclohexane-2(5H)-furanone (2a)$^{3)}$ was formed in a good yield(76%; conversion 100%). The same reaction took place with 3,3-dimethyl-4-methylenedihydro-2(5H)-furanone(1b).$^{4)}$ And the reaction was found to be catalytic with respect to palladium even under N_2 atmosphere. For example, 1b(1.4 mmol) was treated with Pd(diphos)$_2$ (0.04 mmol) at 110 °C for 1.5 h in toluene (2 ml) under N_2 atmosphere(1 atm) to yield 4,5,5-trimethyl-2(5H)-furanone(2b)$^{5)}$ (0.36 mmol, yield 26%, turnover number 9) with 100% conversion. Under CO_2 pressure(60 atm) the yield of 2b increased to 38%. In these reactions the formation of two other products with molecular weight 218 and 390 was also observed by GLC-mass, the structures of which were uncertain.

$Pd(PPh_3)_4$ scarcely catalyzed this reaction.

Although we are not certain the exact pathway of this reaction, the scheme involving a trimethylenemethane complex of the type 3 as an intermediate is a possible one.

References

1) For example, B. M. Trost, "Organopalladium Intermediate in Organic Synthesis" (Tetrahedron Report No. 32), Pergamon Press(1978).

2) This compound was synthesized[6)] by the reaction of cyclohexylidenecyclopropane and CO_2 in the presence of $Pd(PPh_3)_4$.

3) IR(neat) 1740(C=O), 1640(C=C), 1210(C-O), and 850(HC=C) cm^{-1}. NMR(CCl_4) δ 1.0-1.9(10 H, br, $-CH_2-$), 1.95(3 H, d, J=1.5 Hz, $CH_3C=C$), and 5.5(1 H, q, J=1.5 Hz, CH=C). The yield was determined by GLC.

4) This compound was synthesized[6)] by the reaction of isopropylidenecyclopropane and CO_2 in the presence of $Pd(PPh_3)_4$.

5) Mp 44.5-45.5 °C (lit[7)] 44.5-46.5 °C). IR(KBr) 1750 and 1730(branched C=O), 1640 (C=C), and 1280(C-O) cm^{-1}. NMR(CCl_4) δ 1.35(6 H, s, CH_3), 2.0(3 H, d, J=1.4 Hz, $CH_3C=C$), and 5.55(1 H, q, J=1.4 Hz, HC=C). UV_{max}(EtOH) 206 nm(ε16,300). Found: C, 65.71; H, 7.93%. Calcd for $C_7H_{10}O_2$: C, 66.65; H, 7.99%.

6) Y. Inoue, T. Hibi, M. Satake, and H. Hashimoto, J. Chem. Soc. Chem. Commun., 1979, 982.

7) J. M. Stewart and D. W. Wooley, J. Am. Chem. Soc., 81, 4951(1959).

(Received September 4, 1980)