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# SYNTHESIS OF UNSATURATED BUTYROLACTONES BY PALLADIUM CATALYZED INTRAMOLECULAR CARBOALKOXYLATION OF HOMOALLYLIC CHLOROFORMATES

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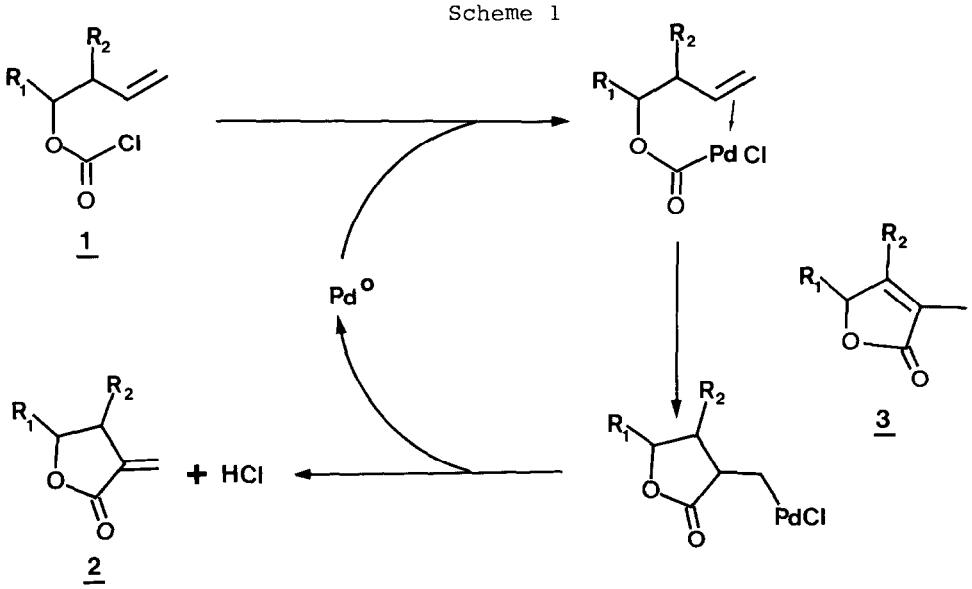
*Summary : We propose a new method for the preparation of α-methylene lactones involving the palladium (o) catalyzed cyclisation of homoallylic chloroformates 1.*

Naturally occuring unsaturated lactones and especially α-methylene-γ-butyrolactones have attracted considerable attention from a synthetic point of view (1). The organometallic methods proposed for the construction of the α-methylene-lactone skeleton consist of the carbonylation of halovinylic(2,3) or homopropargylic (4,5) alcohols induced by Nickelcarbonyl or palladium catalysts. However most of these methods are stoechiometric (2,4) or need more than two steps for preparation of starting materials (2-5). The carbonylation of homopropargylic alcohols via Pd(II) catalysts involves a carboalkoxypalladium intermediate : $L_2Pd\ X\ (CO_2R)$ ; such a species, when prepared from $ClHgCO_2CH_3$ and $PdCl_2$ is able to produce the carboalkoxylation of activated alkenes (6) despite its low reactivity towards olefins, when prepared directly from $ClCO_2CH_3$ and Pd (7). As intramolecular reactions of Pd(II) species with addition on the double bond can lead to cyclised compounds (8), we thought that it would be possible to devise a catalytic process for intramolecular carboalkoxylation of homoallylic chloroformates according to scheme 1.

Scheme 1




The reaction became efficient when the chloroformate and the alkene functions were present in the same molecule (Table). Starting materials 1 were easily prepared from the corresponding homoallylic alcohols (9) and phosgene, then treated under our standard conditions : a solution 0.1 M of chloroformate in anhydrous p.xylene was added under argon into a flask containing sodium bicarbonate (2 equivalents/1), palladium catalyst and where shown in the Table triphenylphosphine, then gradually heated with stirring at 130° during 16 h. After filtration on Celite compounds 2 and 3 were isolated by chromatography.

The table shows that the reaction was very sensitive to the reaction conditions : the best results were obtained when solid sodium bicarbonate was used as the base ; selectivity of the reaction towards α-methylene-butyrolactone required the presence of triphenylphosphine (2 equivalents/Pd).

The main difference with the other organometallic methods consists of the simple way chosen to prepare the reacting intermediate ; furthermore activation of unsaturated chloroformates could not be replaced by cyclocarbonylation of homoallylic alcohols since the reaction of 3-butenol in the presence of CO, $PdCl_2$ and phosphine leads to saturated lactones (5c).

Table : 1 —> 2 + 3

| $R_1$ | $R_2$ | catalyst [a] Molecular ratio/1 | $PPh_3$ | Yield | 2/3 [b] | Turnover |
|---|---|---|---|---|---|---|
| H | H | A (0.02) | 0 | 7[c] | 90/10 | 4 |
| | | A (0.02) | 0.04 | 0 | - | - |
| | | B (0.02) | 0.04 | 0 | - | - |
| $C_2H_5$ | H | A (0.02) | 0.04 | 7 | 100/0 | 4 |
| n.$C_3H_7$ | H | A (0.02) | 0 | 43 | 66/34 | 22 |
| | | A (0.02) | 0.04 | 45 | 100/0 | 23 |
| n.$C_4H_9$ | H | A (0.02) | 0.04 | 50 | 100/0 | 25 |
| n.$C_6H_{13}$ | H | A (0.01) | 0.02 | 26 | 100/0 | 26 |
| | | A (0.02) | 0.04 | 46 | 100/0 | 23 |
| | | A (0.04) | 0.08 | 58 | 100/0 | 15 |
| | | B (0.02) | 0 | 1 | - | 0.5 |
| | | B (0.02) | 0.04 | 52 | 100/0 | 26 |
| | | C (0.04) | 0.08 | 32 | 100/0 | 16 |
| cyclohexyl trans [d] | | A (0.035) | 0.07 | 10 | 100/0 | 3 |
| | | B (0.035) | 0.07 | 36 | 100/0 | 10 |
| cyclohexyl cis [d] | | B (0.04) | 0.08 | 12 | 100/0 | 3 |

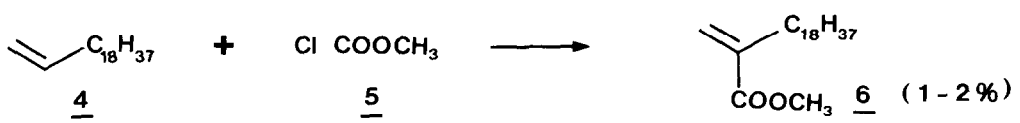
a - A = $Pd(PPh_3)_4$ freshly prepared or recristallyzed ; B = $Pd_2(dba)_3\ CHCl_3$ ; C = $Pd(dba)_2$ ; dba = dibenzylidene acetone

b - determined by $^1H$ NMR. Spectroscopic properties of compounds 2 or 3 were identical with those of the literature (10)

c - 49 % of di (3-butenyl)carbonate isolated beside the lactone

d - T = 80°C.

In contrast to the observed cyclization reaction, we obtained very poor yields of its intermolecular equivalent :



## References and Notes


1) P.A. GRIECO, Synthesis, 67 (1975)
Y.S. RAO, Chem. Rev., 76, 624 (1976).

2) a. I. MATSUDA, Chem. Lett., 773 (1978)
b. M.F. SEMMELHACK and S.J. BRICKNER, J. Org. Chem., 46, 1723 (1981)
c. M.F. SEMMELHACK and S.J. BRICKNER, J. Amer. Chem. Soc., 103,3945 (1981)
d. B.M. TROST and B.P. COPPOLA, J. Amer. Chem. Soc., 104, 6879 (1982).

3) a. A. COWELL and J.K. STILLE, J. Amer. Chem. Soc., 102, 4193 (1980)
b. L.D. MARTIN and J.K. STILLE, J. Org. Chem., 47, 3630 (1982).

4) a. E.R.H. JONES, T.Y. SHEN and M.C. WHITING, J. Chem. Soc., 230 (1950)
b. E.R.H. JONES, G.H. WHITHAM and M.C. WHITING, J. Chem. Soc.,4628 (1957).

5) a. T.F. MURRAY, V. VARMA and J.R. NORTON, J. Amer. Chem.Soc.,99,8085(1977)
b. T.F. MURRAY and J.R. NORTON, J. Amer. Chem. Soc., 101, 4107 (1979)
c. T.F. MURRAY, E.G. SAMSEL, V. VARMA and J.R. NORTON, J. Amer. Chem. Soc. 103, 7520 (1981).

6) R.F. HECK, J. Amer. Chem. Soc., 94, 2712 (1972).

7) S. OTSUKA, A. NAKAMURA, T. YOSHIDA, M. NARUTO and K. ATAKA, J. Amer. Chem. Soc., 95, 3180 (1973).

8) a. Y. ITO, H. AOYAMA, T. HIRAO, A. MOCHIZUKI and T. SAEGUSA, J. Amer. Chem. Soc., 101, 494 (1979)
b. A.S. KENDE, B. ROTH and P.J. SANFILIPPO, J. Amer. Chem. Soc., 104, 1784 (1982)
c. M. MORI, I. ODA and Y. BAN, Tetrahedron Letters, 5315 (1982).

9) a. J.A. KATZENELLENBOGEN and R.S. LENOX, J. Org. Chem., 38, 326 (1973)
b. C. HUYNH, F. DERGUINI-BOUMECHAL and G. LINSTRUMELLE, Tetrahedron Letters, 1503 (1979).

10) For example : a. R.M. CARLSON, Tetrahedron Letters, 111 (1978)
b. M. FRANCK-NEUMANN and C. BERGER, Bull. Soc. Chim. Fr., 4067 (1968)
c. A.D. HARMON and C.R. HUTCHINSON, J. Org. Chem., 40, 3474 (1975).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