Tetrahedron Letters, Vol.32, No.36, pp 4703-4704, 1991
Printed in Great Britain

0040-4039/91 $3.00 + .00
Pergamon Press plc

Direct Synthesis of Lactones by Double Carbonylation of (2-Bromoethyl)benzene Catalyzed by $Sn(Co(CO)_4)_4$

Eric Monflier, Sylvain Pellegrini, André Mortreux* and Francis Petit*

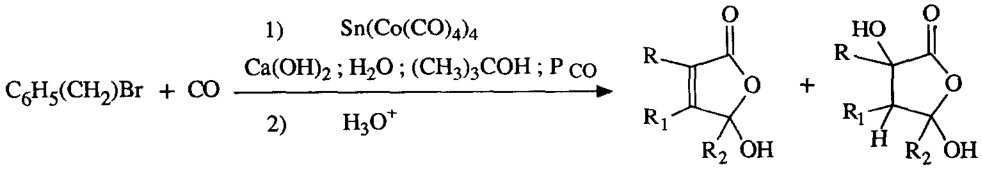
Laboratoire de Chimie Organique Appliquée associé au CNRS
Ecole Nationale Supérieure de Chimie de Lille
B.P. 108 - 59659 Villeneuve d'Ascq, France

Key-words: Double carbonylation, Sn-Co catalyst, lactone synthesis, (2-bromoethyl)benzene.

Abstract: *The direct synthesis of lactones is performed by double carbonylation of (2-bromoethyl)benzene under carbon monoxide pressure. The reaction is catalyzed by $Sn(Co(CO)_4))_4$ in the presence of a base in hydro-alcoholic medium.*

Double carbonylation reactions have been largely investigated during these last years.[1] Thus, double carbonylation of (2-bromoethyl)benzene **1** to benzylpyruvic acid $C_6H_5(CH_2)_2COCO_2H$ **2** is catalyzed with good yield and selectivity by $Co_2(CO)_8$ at 85°C under 65 bar of carbon monoxide.[2]

We now report that in contrast with $Co_2(CO)_8$ (Table), the use[3] of $Sn(Co(CO)_4)_4$, which can be considered as a source[4] of $Co_2(CO)_8$, gives rise during double carbonylation to the selective production of lactones **3** and **4** rather than **2**, according to eq. 1.



1 **3** **4** (1)

R = $C_6H_5(CH_2)_2$- ; R_1 = $C_6H_5CH_2$- ; R_2 = -COOH

In a typical experiment, 7 mL (51 mmol) of **1**, 30 mL (0.32 mol) of 2-methyl-2-propanol, 0.8 g (1 mmol) of $Sn(Co(CO)_4)_4$, 10 g (0.13 mol) of calcium hydroxide and 80 mL (4.5 mol) of water are introduced under nitrogen in a 300 mL stainless steel autoclave, which is pressurized at 65 bar at room temperature and stirred for 16 hours at 85 °C. The reaction mixture is cooled to room temperature, depressurized and filtered. The crude cake is washed with 10 mL of water and 3 x 10 mL of diethylether to give a white solid, which is acidified with a 0.1 N HCl solution and extracted with diethylether. The solution is dried over anhydrous $MgSO_4$ and evaporated. The solid products mixture is then analyzed.[5]

Table. Catalytic double carbonylation of **1** under various conditions.

Entry	Catalyst	Base	PCO (bar)	Yield (%) ^{a}	
				2	**3 + 4** ^{b}
1	$SnCl_2$	LiOH	20	0	0
2	$Co_2(CO)_8$	LiOH	20	35	0
3	$Sn(Co(CO)_4)_4$	LiOH	20	25	0
4	$Co_2(CO)_8$	$Ca(OH)_2$	65	70	0
5	$Sn(Co(CO)_4)_4$	$Ca(OH)_2$	20	traces	57
6	$Sn(Co(CO)_4)_4$	$Ca(OH)_2$	65	traces	67
7	$Co_2(CO)_8 + SnCl_2$	$Ca(OH)_2$	65	traces	65

(a) isolated yield ; (b) the ratio **3** / **4** depends on acidification conditions ; Sn = 1 mmol ; Co = 4 mmol ; LiOH = 0.26 mol ; $Ca(OH)_2$ = 0.13 mol ; $C_6H_5(CH_2)_2Br$ = 51 mmol ; T = 85°C ; t = 16 h.

The synthesis of a lactone similar to **3** ($R = R_1 = CH_3$, $R_2 = C_5H_{11}$) has already been reported from dimethylmaleic anhydride and the Grignard compound of pentyl chloride.[6] It has to be noticed that the selective synthesis of **3** and **4** is only observed when $Ca(OH)_2$ is used, **2** being the only product obtained if an alkaline base like LiOH is used. Further experiments have shown that the lactones are quantitatively transformed into **2** by treatment at 80°C in hydro-alcoholic medium with LiOH or NaOH,whereas this reaction does not occur with $Ca(OH)_2$, as expected. Furthermore, we have observed that $SnCl_2$, as well as $Sn(Co(CO)_4)_4$, induces the synthesis of lactones **3** and **4** from **2** in the presence of $Ca(OH)_2$ in hydro-alcoholic medium. A spectroscopic study performed on the white solid obtained before acidification has revealed that ν (c=o) lactones vibrations are not detected. This shows, as described in the literature[6], that the cyclisation reactions and the dehydratation leading to **3** and **4** occur during the acidic workup.

These experiments demonstrate the bifunctional character of the bimetallic compound $Sn(Co(CO)_4)_4$, generating tetracarbonylcobaltate anions (responsible for synthesis of **2** as calcium salt) and concommitantly a tin species which promotes an aldol condensation[7] between the two $RCOCOO^-$ fragments bound to Ca^{2+}. If an alkaline base like LiOH is used, a retrograde aldol condensation can take place in the course of the reaction and **2** is the only final product (entry 3).[8]

ACKNOWLEDGMENTS

The authors gratefully acknowledge S.N.P.E. for its financial support.

REFERENCES AND NOTES

1. For a review see Collin, J. *Bull. Soc. Chim. Fr.* **1988**, *6*, 976-981. (55 References)
2. Fell, B.; Chrobaczeck, H.; Kohl, W. *Chem.Zeitung* **1985**, *109*, 167-170.Lee, J.Y.; Wolfram, J. U.S. Pat. 4, 492, 798 (**1984**).
3. We have recently described the synthesis and uses of $Sn(Co(CO)_4)_4$ in several reactions: Cabrera, A.; Samain, H.; Mortreux, A.; Petit, F.; Welch, A.J. *Organometallics* **1990**, *9*, 959-964. Cabrera, A.; Mortreux, A.; Petit, F. *J. Mol. Catal.* **1981**, *47*, 11-15.
4. Samain, H.; Carpentier, J.F.; Mortreux, A.; Petit, F. *New J. Chem.* **1991**, *15*, 367-371.
5. Some selected characteristics are listed below: **3**: 2(3-(2-benzene)ethyl-4-benzyl-5-carboxylic acid-5-hydroxy) furanone; I.R.: 3436 (OH), 1735 (COOR), 2400-3200 (COOH) cm^{-1}. MS / FAB^+ high resolution (CH_3OH / Glycerol): 339 (M + H) (Molecular weight obtained by peak matching: 339.1257 ; calculated for $C_{20} H_{19} O_5$ = 339.1232), 294 ((M + H)-COOH), 277 ((M + H)-COOH,-OH).^{13}C NMR (DMSO-d_6): δ 169.67, 168.19, 137.1, 130.12, 85.91, 35.27, 29.07, 28.87. ^1H NMR (DMSO-d_6): δ 3.81 (d, J = 15.1 Hz, 1H), 3.45 (d, J = 15.1 Hz, 1H), 2.4-2 (m, 4H). **4**: 2-oxo-3-(2-benzene)ethyl-3-hydroxy-4-benzyl-5-carboxylic acid-5-hydoxy tetrahydrofuran ; I.R.: 3430 (OH), 3331 (OH), 1775 (COOR), 2400-3200 (COOH) cm^{-1}. MS / FAB^+ (CH_3OH, Glycerol): 357 (M + H), 340 ((M + H)-OH), 323 ((M + H)-(2 x OH)), 312 ((M + H)-COOH), 295 ((M + H) -COOH, -OH). ^{13} C NMR (DMSO-d_6): δ 176.35, 168.97, 99.38, 75.28, 53.03 , 35.95, 28.85, 28.67. ^1H NMR (DMSO-d_6): δ 3.2 (m, 1H), 2.9-2.65 (m, 4H), 2.15-1.95 (m, 2H).
6. Lardelli, G.; Dijkstra, P.; Harkes, D.; Boldingh, J. *Rec. Trav. Chim.* **1966**, *85*, (1), 43-55 and references therein.
7. Kobayashi, K.; Kawanisi, M.; Hitomi, T.; Kozima, S. *Chem. Lett.* **1983**, 851-854. Stevens, R.W.; Mukaiyama, T.; Iwasawa, N. *Chem. Lett.* **1982**, 353-356.
8. The experiment 3, stopped after 2 hours (c.a. 13 % yield), has given a mixture of **2**, **3**, **4**, as indicated by I.R. spectroscopy.

(Received in France 31 May 1991)