Tetrahedron Letters,Vol.27,No.44,pp 5389-5392,1986 0040-4039/86 $3.00 + .00
Printed in Great Britain Pergamon Journals Ltd.

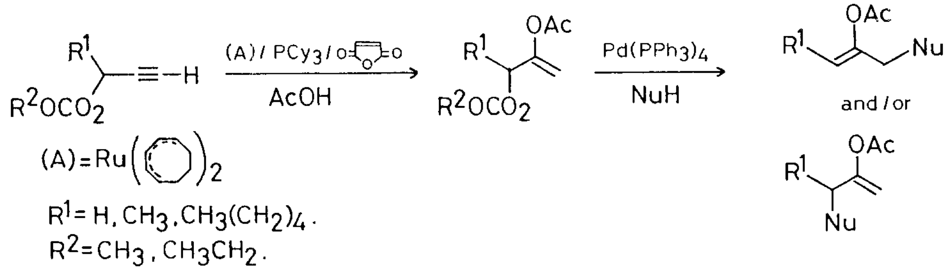
RUTHENIUM-CATALYZED SYNTHESIS OF 2-ACETOXYALLYL CARBONATES: A SYNTHON FOR PALLADIUM-CATALYZED 2-ACETOXYALLYLATION OF CARBONUCLEOPHILES

Yoji Hori, Take-aki Mitsudo,* and Yoshihisa Watanabe*
Department of Hydrocarbon Chemistry, Faculty of Engineering,
Kyoto University, Sakyo-ku, Kyoto 606, Japan

Summary: Propargyl carbonates react with acetic acid in the presence of a catalytic amount of bis(η^5-cyclooctadienyl)ruthenium/PCy_3/maleic anhydride at 80 °C to give 2-acetoxyallyl carbonates in good yields with excellent regioselectivity. These 2-acetoxyallyl carbonates catalytically react with carbonucleophiles in the presence of tetrakis(triphenylphosphine)palladium to give 2-acetoxyallylated products in good to excellent yields.

Although ruthenium-catalyzed organic synthesis is in progress,$^{1)}$ it is far behind the chemistry of palladium.$^{2)}$ We now report an example which suggests that to join the chemistry of ruthenium to that of palladium would provide a fruitful field in organic synthesis. Recently, we reported a novel selective addition of carboxylic acids to terminal acetylenes catalyzed by bis(η^5-cyclooctadienyl)ruthenium/PR_3/maleic anhydride.$^{3)}$ On the other hand, allylic carbonates have been found to be useful reagents for palladium-catalyzed allylation under neutral conditions.$^{4)}$ Combination of the ruthenium-catalyzed selective addition of acetic acid to propargyl carbonates and the palladium-catalyzed 2-acetoxyallylation of carbonucleophiles provides a new method of the synthesis of novel polyfunctional enol esters (Scheme), the preliminaly results of which are described below.

Scheme



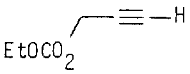
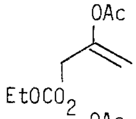
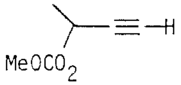
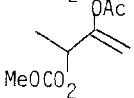
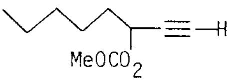
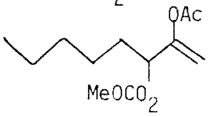
Ruthenium catalyzed addition of acetic acid to propargyl carbonate.

In the presence of a catalytic amount of the complex (A)/PCy_3/maleic anhydride, the addition of acetic acid to propargyl carbonates gave the corresponding 2-acetoxyallyl carbonates as a sole product in yields of 40-63 %. Representative results are summarized in Table 1. When tricyclohexylphosphine was used as a ligand, an excellently high regioselectivity was achieved.

In a typical procedure, a mixture of ethyl propargyl carbonate (1.28 g, 10 mmol), acetic acid (5.0 ml), bis(η^5-cyclooctadienyl)ruthenium (A) (0.032 g, 0.1 mmol), tricyclohexylphosphine (0.056 g, 0.2 mmol), maleic anhydride (0.020 g, 0.2 mmol) was stirred under an argon atmosphere at 80 °C for 8 h. Careful vacuum distillation of the reaction mixture afforded 1.18 g (yield 63 %) of ethyl 2-acetoxy-2-propenyl carbonate **1** (Table 1, run 1). Other reactions were carried out in the similar manner. All products were characterized spectroscopically and by satisfactory analytical data.

The successful selective synthesis of 2-acetoxyallyl carbonates which have not been synthesized by other methods led us to apply this synthon to palladium-catalyzed allylation of carbonucleophiles found by Tsuji and his co-workers.[4)]

Table 1 Selective Addition of Acetic Acid to Propargyl Carbonates[a)]

run	carbonate	temp.(°C)	time(h)	product		yield[b)] (%)	regio-selectivity(%)
1		80	8		**1**	63 (65)	99[c)]
2		80	8		**2**	44	100
3		80	10		**3**	40	100

a) Reactions were carried out using carbonate (10 mmol), complex (A) (0.1 mmol), PCy_3 (0.2 mmol), maleic anhydride (0.2 mmol) in acetic acid (5.0 ml) under argon.

b) Isolated yield (GLC yield).

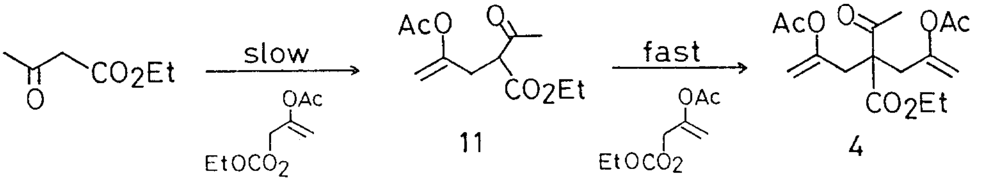
c) When PBu_3 was used in place of PCy_3, 2-acetoxyallyl ethyl carbonate was also formed and the regioselectivity was 90 %.

2-Acetoxyallylation catalyzed by tetrakis(triphenylphosphine)palladium.

In the presence of a catalytic amount of tetrakis(triphenylphosphine)palladium, 2-acetoxyallyl carbonates readily reacted with carbonucleophiles.

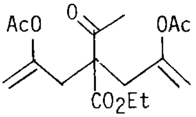
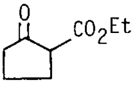
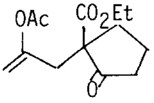
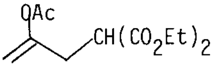
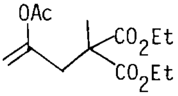
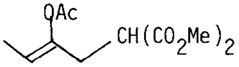
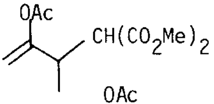
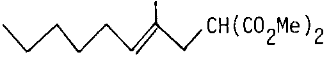
In a typical procedure, a mixture of ethyl 2-acetoxy-2-propenyl carbonate **1** (0.94 g, 5 mmol), ethyl 2-oxocyclopentanecarboxylate (0.78 g, 5 mmol), tetrakis(triphenylphosphine)palladium (0.23 g, 0.2 mmol), tetrahydrofuran (10.0 ml) as solvent was stirred under an argon atmosphere at 23 °C for 6 h. Careful vacuum distillation of the reaction mixture afforded 1.17 g (yield 92 %) of **5** (Table 2, run 2). Representative results are summarized in the Table 2. Ethyl acetoacetate smoothly reacted with two equivalents of carbonate **1** to give doubly acetoxyallylated compound **4** in a yield of 86 % selectively (run

1). Since 2-acetoxyallylated compound **11** reacts faster than ethyl acetoacetate with carbonate **1**, it is difficult to obtain the compound **11** selectively (eq. 1). Diethyl malonate also reacted with the carbonate **1** to give 2-acetoxyallylated compound **6** in a yield of 77 % (run 3). The reaction of the carbonate **1** with diethyl 2-methylmalonate afforded the product **7** in a yield of 34 % (run 4). Carbonates **2** and **3** also reacted with dimethyl malonate to give the corresponding products **8**, **9** (53 %, **8**/**9**=2, run 5) and **10** (56 %, run 6), respectively. The



(1)

Table 2 Reaction of 2-Acetoxyallyl Carbonates with Carbonucleophiles[a)]

run	carbonate (mmol)	nucleophile (mmol)	cat. (mmol)	temp. (°C)	time (h)	product		yield[b)] (%)
1	**1** (10)	$CH_3COCH_2CO_2Et$ (5)	0.1	60	7		**4**	86
2	**1** (5)	 (5)	0.2	23	6		**5**	92
3	**1** (5)	$CH_2(CO_2Et)_2$ (15)	0.1	17	3		**6**	77
4	**1** (10)	$CH_3CH(CO_2Et)_2$ (5)	0.2	60	53		**7**	34
5	**2** (5)	$CH_2(CO_2Me)_2$ (15)	0.1	50	6	 	**8** **9**	53 **8**/**9**=2
6	**3** (5)	$CH_2(CO_2Me)_2$ (15)	0.2	60	7		**10**	56

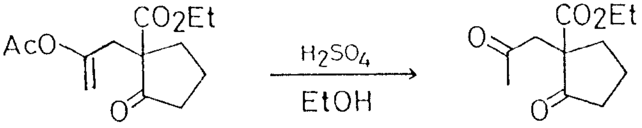
---

a) Reactions were carried out using $Pd(PPh_3)_4$ in THF (10 ml) as solvent under argon.

b) Isolated yield.

products **1-10** are novel polyfunctional enol esters and they would be utilized as intermediates for further organic syntheses such as cyclization or as the precursors of enolate anions.[5)]

Ethanolysis of **5** in the presence of a catalytic amount of 96 % H_2SO_4 gave 1,4-diketone **12** in a yield of 95 % (eq. 2).



5

12
95 %

(2)

Thus the combination of the ruthenium-catalyzed addition of acetic acid to propargyl carbonates and the palladium-catalyzed 2-acetoxyallylation reaction provides a novel method for the preparation of the new and useful polyfunctional enol esters.

Further studies on the scope and synthetic application of the 2-acetoxyallylation are now in progress.

This work was partly supported by a Grant-in-aid from the Ministry of Education, Science and Culture (No. 61225012 and 61550634).

References

1) For example: (a) Bennett, M. A.; Matheson,T. W. Comprehensive Organometallic Chemistry, **1982**, 4, 931. (b) Mitsudo, T.; Nakagawa, Y.; Watanabe, K.; Hori, Y.; Misawa, H.; Watanabe, H.; Watanabe, Y. J. Org. Chem. **1985**, 50, 565. (c) Rotem, M.; Shvo, Y. Organometallics, **1983**, 2, 1689. (d) Tsuji, Y.; Huh, K. -T.; Ohsugi, Y.; Watanabe, Y. J. Org. Chem. **1985**, 50, 1365. (e) Murahashi, S. -I.; Naota, T.; Taki, H. J. Chem. Soc., Chem. Commun. **1985**, 613.

2) (a) Tsuji, J. "Organic Synthesis with Palladium Compounds", Springer-Verlag, Berlin, 1980. (b) Tsuji, J. J. Organomet. Chem. **1986**, 300, 281. (c) Trost, B. M. Acc. Chem. Res. **1980**, 13, 385. (d) Trost, B. M. J. Organomet. Chem. **1986**, 300, 263. (e) Heck, R. F. "Palladium Reagents in Organic Syntheses", Academic Press, London,1985.

3) (a) Mitsudo, T.; Hori, Y.; Watanabe, Y. J. Org. Chem. **1985**, 50, 1566. (b) Mitsudo, T.; Hori, Y.; Watanabe, Y. Tetrahedron Lett. **1986**, 27, 2125.

4) Minami, I.; Shimizu, I.; Tsuji, J. J. Organomet. Chem. **1985**, 296, 269 and references cited therein.

5) House, H. O. "Modern Synthetic Reactions" Second Edition, W. A. Benjamin, Inc., Menlo Park, California, 1972, PP 773-776.

(Received in Japan 8 July 1986)