Tetrahedron Letters,Vol.27,No.52,pp 6323-6324,1986 0040-4039/86 $3.00 + .00
Printed in Great Britain Pergamon Journals Ltd.

SYNTHESIS OF ENOL ESTERS FROM TERMINAL ALKYNES CATALYZED BY RUTHENIUM COMPLEXES

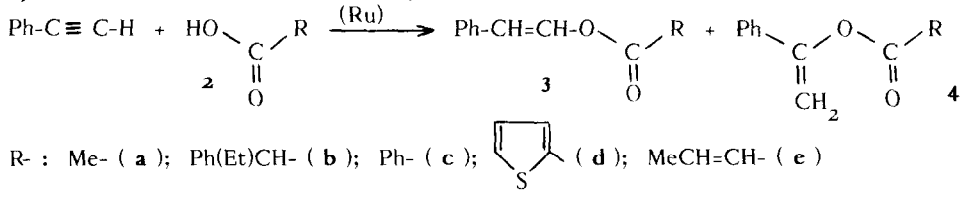
Christophe Ruppin and Pierre H. Dixneuf

Laboratoire de Chimie de Coordination Organique - U.A. CNRS 415
Campus de Beaulieu, Université de Rennes, 35042 Rennes (France)

Summary *: Regioselective enol ester formation results from the addition of saturated and unsaturated carboxylic acids to phenylacetylene in the presence of* $RuCl_3$, $RuCl_3/2PR_3$ *or* $RuCl_2(PMe_3)$*(arene) catalysts.*

Mononuclear ruthenium complexes, such as $RuCl_3$ or $RuCl_2(PR_3)$(arene), have been shown recently to be more efficient catalysts than $Ru_3(CO)_{12}$ for the addition of ammonium carbamates to terminal akynes in the synthesis of vinyl carbamates.[1] As enol esters, which can be obtained from the addition of carboxylic acids to vinylmercury(II) derivatives[2], were shown to be useful precursors for the functionalization of substrates[3] it appeared interesting to investigate whether these ruthenium complexes could also perform the addition of carboxylic acids to alkynes giving the corresponding enol esters. Very recently, unsaturated carboxylic acids were shown to add to alkynes[4b] and the addition of saturated carboxylic acids to hex-1-yne[4a], using a Ru(η^5-cyclooctadienyl)$_2$/ maleic anhydride system as catalyst, has been described. This leads us to report our preliminary results on the addition of a variety of carboxylic acids to phenylacetylene, using easily accessible mononuclear ruthenium catalysts.

$RuCl_3,3H_2O$ **1a** and $RuCl_2(PMe_3)$(p-cymene) **1b** catalyze the addition to phenyl acetylene of saturated carboxylic acids such as acetic **2a** and 2-phenylbutyric **2b** acids and α, β-unsaturated carboxylic acids such as benzoic **2c**, 2-thiophene carboxylic **2d**, and crotonic **2e** acids.



R- : Me- (**a**); Ph(Et)CH- (**b**); Ph- (**c**); (**d**); MeCH=CH- (**e**)

Complex **1b** catalyzes the addition of both saturated (runs 4, 8) and unsaturated (run 12) carboxylic acids to phenylacetylene. The enol ester **4** is always obtained with a good selectivity.

In a typical experiment, acid **2b** (1.64 g, 10 mmol), phenylacetylene (1.02 g, 10 mmol) and complex **1b** (76.4 mg, 0.2 mmol) were dissolved in 20 ml of ethylbenzene in a Schlenk tube. The mixture was heated for 15 h at 120°C. The residual acid **2b** was extracted using $NaHCO_3$ aqueous solution and the esters were obtained *via* distillation (1.5 g, 56 %) (run 8).

In contrast, if **1a** also catalyzes the addition of both saturated and unsaturated acids to phenylacetylene, the (E)-3 isomer is then obtained as the major product (runs 1, 5, 9, 13, 15).

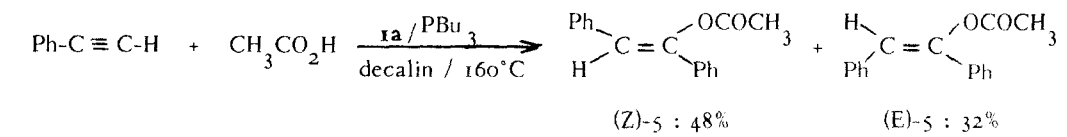
Table : Synthesis of enol esters from phenylacetylene and ruthenium catalyst **1**[a,b]

Run	acid	Ru	PR_3	ester 4	Yield % 3Z	3E	Run	acid	Ru	PR_3	ester 4	Yield % 3Z	3E
1	(2a)	**1a**	---	3	20	61	9	(2c)	**1a**	---	6	18	61
2	"	**1a**	PBu_3	54(46)	11	8	10	"	**1a**	PBu_3	63	1	7
3	"	**1a**	PCy_3	36	5	1	11	"	**1a**	PMe_3	73	-	1
4	"	**1b**	---	46	10	10	12	"	**1b**	---	68(61)	-	4
5	(2b)	**1a**	---	6	24	61	13	(2d)	**1a**	---	28	21	38
6	"	**1a**	PBu_3	44	3	1	14	"	**1a**	PBu_3	52	12	4
7	"	**1a**	PCy_3	31	1	-							
8	"	**1b**	----	61(56)	6	2	15	(2e)	**1a**	---	5	17	56

(a) (Ru) : **1a** ($RuCl_3$, $3H_2O$) ; **1b** ($RuCl_2(PMe_3)$(p-cymene); (b) Phenylacetylene (10 mmol); acid (10 mmol); **1** (0.2 mmol); PR_3 (0.4 mmol); ethylbenzene (20 ml); 120°C, 15 h. (c) GLC yields and ( ) isolated yields.

When two equivalents of a basic and bulky phosphine such as PMe_3, $P(n\text{-}Bu)_3$ and PCy_3 (runs 2 and 3 ; 6 and 7 ; 10 and 11 ; 14). The conversion is always high (90-100 %) but when a phosphine was added, the parallel formation of the alkyne dimer PhCH=CHC≡CPh (E + Z) occurs and undergoes to a decrease of the yield in enol esters.

The catalytic systems do not appear to be specific of terminal alkynes, $RuCl_3$ **1a** with PBu_3 also catalyzed the addition of acetic acid to diphenylacetylene, as it was already observed using $Ru_3(CO)_{12}$[5] as catalyst.



(Z)-5 : 48% (E)-5 : 32%

Authors are grateful to CNRS and SNPE for a research grant to C.R. and for financial support.

References

1) (a) Sasaki, Y ; Dixneuf, P.H. ; J. Chem. Soc. Chem. Commun. 1986, 790. (b) Mahé, R. ; Dixneuf, P.H. ; Lécolier, S. Tetrahedron Lett., accepted for publication.

2) (a) Larock, R.C. : Oertle, K ; Beatty, K.M. ; J. Am. Chem. Soc. 1980, 102, 1966 and references therein. (b) Bach, R.D. ; Woodard, R.A. ; Anderson, T.J. ; Glick, M.D. ; J. Org. Chem. 1982, 47, 3707.

3) (a) Waxler, A. ; Balchunis, R.J. ; Swenton, J.S. ; J. Chem. Soc. Chem. Commun. 1975, 601. (b) Rothman, E.S. ; Moore, G.G. ; J. Org. Chem. 1970, 35, 2351. (c) Wasserman, H.H. ; Wentland, S.H. ; J. Chem. Soc. Chem. Commun. 1970, 1.

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

5) Rotem, M. ; Shvo, Y. ; Organometallics, 1983, 2, 1689.

(Received in France 19 September 1986)