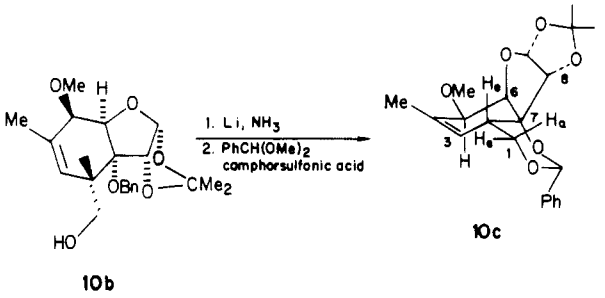
Scheme III



to a readily prepared derivative of "diacetone glucose", whereby the oxahydrindene **2** is obtained optically active, with the correct stereochemistry, and appropriately functionalized for further elaboration.

The known[14] allylic alcohol **3a** was prepared from diacetone glucose, and standard operations on the corresponding benzyl ether **3b** were applied to methylate the C5 hydroxyl group (glucose or avermectin numbering) and to expose the primary hydroxyl group in **4d**.[15] Swern oxidation[16] gave the aldehyde **5a**, and a Henry reaction, followed by sulfonation and β-elimination led to the nitroalkene **5b** which underwent conjugate addition with methyllithium to afford the epimeric mixture **6** (Scheme I).

The prospective INOC reaction[13] was the key step in our sequence, and the stereochemistry thereof was central to our plans, since the crucial C2 center of **1** is created in this process. Of the possible modes of cyclization, X and Y, shown in Scheme II, the former seemed more likely, since it proceeds through a chair transition state. In the event, treatment of **6** under the Mukaiyama conditions for generating a nitrile oxide[17] *yielded 7 as single C2 isomer* (74%) whose reduction, under the conditions prescribed by Curran,[18] afforded ketone **8** which was processed without event to the methanesulfonate **9**. The regioselectivity of the up-coming β-elimination was an obvious point of speculation; however, conditions were found where a single olefin, **10a**, was obtained.

Although the above transition-state analysis (Scheme II) seemed rational, it was essential to establish the C2 configuration unambiguously. Accordingly **10b** was converted into the benzylidene derivative **10c** as outlined in Scheme III. The 250-MHz ^{1}H NMR spectrum of **10c** shows the H1 protons at 4.34 and 4.22 ppm with couplings of 3.9 and 0.0 Hz, respectively, to H2. With respect to the benzylidene ring, the latter data rule out trans diaxial relationships, and given the fact that the C7 configuration is known, the parameters can *only* be accommodated by the representation shown in Scheme III.

After protecting group adjustments, the Gray procedure for reductive cleavage of glycosides[19] was then applied to **10b** and to the corresponding hemiacetal obtained by hydrolysis of the acetonide; but in both cases, complex mixtures resulted. A less direct procedure was therefore employed involving the triol **11**, which underwent sulfonation in the presence of pyridine to give **12**[15] directly. Oxidation to compound **2**[15] followed.

The INOC route illustrated in Scheme I has been shown to provide a simple secure route to the oxahydrindene **2**, and given the ready availability of the starting material **3a**, a variety of analogues of **2** can be readily envisaged. Studies along this line are underway and will be reported in due course.

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Mahavir Prashad, Bert Fraser-Reid*
Paul M. Gross Chemical Laboratory
Duke University
Durham, North Carolina 27706
Received October 23, 1984

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Selective Addition of Unsaturated Carboxylic Acids to Terminal Acetylenes Catalyzed by Bis(η^5-cyclooctadienyl)ruthenium(II)-Tri-*n*-butylphosphine. A Novel Synthesis of Enol Esters

Summary: Unsaturated carboxylic acids such as methacrylic acid, crotonic acid, vinylacetic acid, and sorbic acid and aromatic carboxylic acids reacted with terminal acetylenes in the presence of a catalytic amount of bis(η^5-cyclooctadienyl)ruthenium-P-*n*-Bu_3 in benzene at 80 °C to give enol esters having a terminal methylene group in excellent yields with high regioselectivity.

Sir: Enol esters have proven to be extremely valuable intermediates in organic synthesis.[1] Major methods for preparing enol carboxylates are (1) conversion of ketones or aldehydes into enolates followed by their treatment with acylating agents,[2] (2) the palladium-promoted acetoxylation of olefins,[3,4] and (3) addition of carboxylic acids to alkynes.[5] The last one is known to be catalyzed by mercury salts and strong acids[5a] or Lewis acids.[5b] In many cases stoichiometric quantities of mercury salts are used.[6,7] Recently, addition of carboxylic acids to internal alkynes catalyzed by $Ru_3(CO)_{12}$ and $[Ru(CO)_2(CH_3CO_2)]_n$ at 145 °C was reported.[8]

We now report a novel selective synthesis of enol esters through the addition of unsaturated carboxylic acids to

(1) For example: (a) Rozen, S.; Lerman, O. *J. Am. Chem. Soc.* **1979**, *101*, 2782. (b) Wexler, A.; Balchunis, R. J.; Swenton, J. S. *J. Chem. Soc., Chem. Commun.* **1975**, 601. (c) Schmitt, G.; Warwel, S.; Homminga, E.; Meltzow, W. *Justus Liebigs Ann. Chem.* **1972**, *763*, 75.
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(5) For example: (a) Fahey, R. C.; Lee, D. J. *J. Am. Chem. Soc.* **1966**, *88*, 5555. (b) Hudrlik, P. F.; Hudrlik, A. M. *J. Org. Chem.* **1973**, *38*, 4254. (c) Krafft, G. A.; Katzenellenbogen, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 5459. (d) Lemaire, H.; Lucas, H. J. *J. Am. Chem. Soc.* **1955**, *77*, 939. (e) After submission of this manuscript, palladium-catalyzed cyclization of alkynoic acid was reported: Lambert, C.; Utimoto, K.; Nozaki, H. *Tetrahedron Lett.* **1984**, *25*, 5323.
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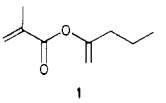
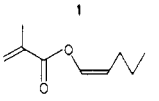
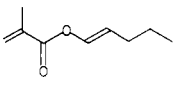
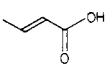
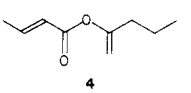
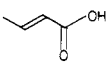
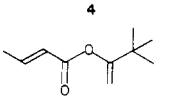
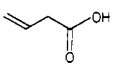
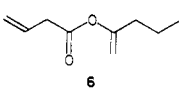
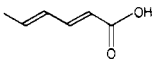
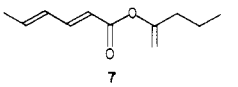
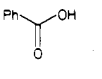
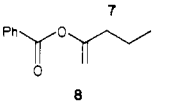
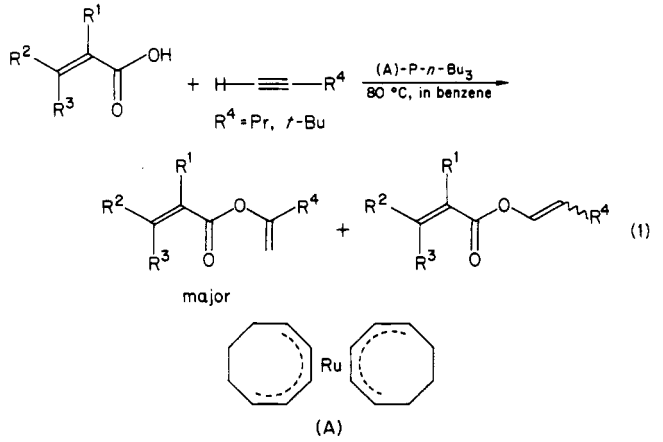
Table I. Addition of Carboxylic Acids to Terminal Acetylenes Catalyzed by Bis(η^5-cyclooctadienyl)ruthenium-P-*n*-Bu_3[a]

run	acid	acetylene	catalyst, mmol	P-*n*-Bu_3, mmol	temp, °C	time, h	product	yield,[b] %
1		1-pentyne		0.2	80	4		
2		1-pentyne	0.1		80	4	 1	8 (5)
							 2	18 (13)
							 3	18 (12)
3		1-pentyne	0.1	0.2	80	4	1	93 (66)
							2	2
							3	2
4		1-pentyne	0.1	0.2	80	4	 4	69 (50)
5		3,3-dimethyl-1-butyne	0.1	0.2	80	4	 5	(68)
6		1-pentyne	0.2	0.4	80	8	 6	(40)
							4	(26)
7		1-pentyne	0.1	0.2	80	4	 7	97 (79)
8		1-pentyne	0.1	0.2	80	4	 8	99 (75)

[a] Carboxylic acid, 10 mmol; acetylene, 10 mmol; benzene, 5.0 mL. [b] Determind by GLC based on the amount of acetylene. Isolated yields are given in parentheses.

terminal acetylenes catalyzed by a two-valent ruthenium complex under mild reaction conditions (eq 1).



Unsaturated acids and benzoic acid readily reacted with 1-pentyne or 3,3-dimethyl-1-butyne in the presence of a catalytic amount of bis(η^5-cyclooctadienyl)ruthenium-(A)–P-*n*-Bu_3 in benzene at 80 °C to give the corresponding enol esters. The results are summarized in Table I.

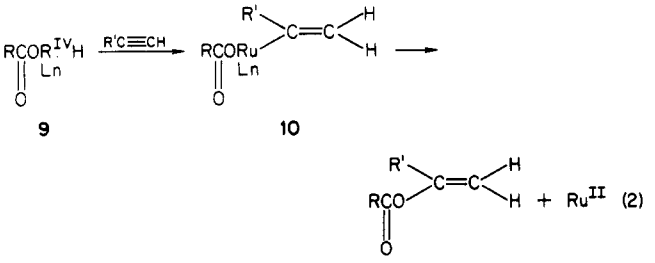
In a typical procedure, a mixture of 2,4-hexadienoic acid (sorbic acid) (1.12 g, 10 mmol), 1-pentyne (0.68 g, 10 mmol), complex A (0.032 g, 0.1 mmol), P-*n*-Bu_3 (0.040 g, 0.2 mmol), and benzene (5.0 mL) was heated in a heavy-walled sealed tube at 80 °C for 4 h. Careful vacuum distillation of the reaction mixture afforded 1.42 g (yield 79%) of 1-penten-2-yl 2,4-hexadienoate (**7**). Other reactions were carried out in the similar manner. All new compounds **1**–**8** were characterized spectroscopically and satisfactory analytical data were obtained.

In the presence of the complex A–2P-*n*-Bu_3, the addition reaction of 2-methyl-2-propenoic acid to 1-pentyne gave the corresponding enol esters **1**, **2**, and **3**; the major enol ester was 1-penten-2-yl 2-methyl-2-propenoate (**1**) in a yield of 93% (run 3). In contrast, in the presence of the complex A without P-*n*-Bu_3, the enol esters **1**, **2**, and **3** were obtained in low yields and the selectivity of them was low (run 2). The reaction of 2-butenoic acid with 1-pentyne and 3,3-dimethyl-1-butyne gave the corresponding enol esters 1-penten-2-yl 2-butenoate (**4**) and 3,3-dimethyl-1-buten-2-yl 2-butenoate (**5**) in 69% and 68% yields, respectively (runs 4 and 5). The addition of 3-butenoic acid to 1-pentyne gave 1-penten-2-yl 3-butenoate (**6**) and its isomer **4** in 40% and 26% yields, respectively (run 6). The reaction of benzoic acid with 1-pentyne also gave 1-penten-2-yl benzoate (**8**) in 99% yield (run 8).

Small amounts of three enol acetates were produced by the addition of acetic acid to 1-pentyne in the presence of

the complex A without P-*n*-Bu_3. However, when P-*n*-Bu_3 was added to the system, the reaction did not occur and the starting materials were recovered.[9] The rate of an addition reaction of carboxylic acids to internal acetylenes such as 3-hexyne under the reaction conditions used was slow.

Although the mechanism of the addition reaction is not clear at the present time, one of the possible routes may be explained by assuming the formation of a hydrido(carboxylate)ruthenium(IV) complex (**9**) by the oxidative addition of a carboxylic acid to a Ru(II) complex[10] and the subsequent insertion of an acetylene into the Ru–H bond giving **10**. The reductive elimination of **10**[11] could afford the enol esters and the Ru(II) species again (eq 2).[12]



(2)

(9) It seems that the catalyst would be converted into an inactive stable complex. In the case of the bis(η^5-cyclooctadienyl)ruthenium–PPh_3–CH_3CO_2H–1-pentyne system, $Ru(PPh_3)_2(CO)_2(OAc)_2$ was isolated from the reaction solution in a fairly good yield.

(10) Oxidative addition of carboxylic acids to Vaska's complex was studied precisely: Deeming, A. J.; Shaw, B. L. *J. Chem. Soc. A* **1969**, 1802.

(11) A reductive elimination of Pd(R)(OAc)Ln has been proposed, ref 6.

Vinyl esters of unsaturated carboxylic acids have been prepared by a replacement of the acetoxy group of vinyl acetate with an unsaturated acyloxy group catalyzed with mercurium salts[13] or palladium salts.[14] Thus the present reaction provides a novel and versatile method of the direct preparation of enol esters of unsaturated carboxylic acids which are useful for various organic syntheses.[1]

Registry No. **1**, 95865-50-2; **2**, 95865-51-3; **3**, 95865-52-4; **4**, 95865-53-5; **5**, 95865-54-6; **6**, 95865-55-7; **7**, 95865-56-8; **8**, 95865-57-9; CH_2=$C(CH_3)CO_2H$, 79-41-4; (*E*)-CH_3CH=$CHCO_2H$, 107-93-7; CH_2=$CHCH_2CO_2H$, 625-38-7; (*E*,*E*)-CH_3CH=$CHCH$=$CHCO_2H$, 110-44-1; $PhCO_2H$, 65-85-0; PBu_3, 998-40-3; 3,3-dimethyl-1-butyne, 917-92-0; 1-pentyne, 627-19-0; bis(η^5-cyclooctadienyl)ruthenium, 63395-36-8.

(12) Other mechanisms including nucleophilic attack of carboxylic acid on the coordinated acetylenes (one of the referees pointed out this mechanism to whom we are indebted) should be discussed to conclude the mechanism of this reaction.

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Take-aki Mitsudo,* Yoji Hori, Yoshihisa Watanabe*

Department of Hydrocarbon Chemistry
Faculty of Engineering
Kyoto University, Sakyo-ku
Kyoto 606, Japan

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