Pergamon

Tetrahedron Letters, Vol. 38, No. 28, pp. 4989-4992, 1997

0040-4039/97 $17.00 + 0.00

PII: S0040-4039(97)01067-8

Novel rhodium-catalyzed cyclic carbonylation of 2-phenylethynylbenzoates leading to indeno[1,2-c]isocoumarin

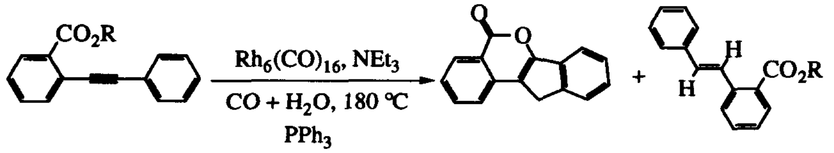
Takashi Sugioka, Eiji Yoneda, Kiyotaka Onitsuka, Shi-Wei Zhang, and Shigetoshi Takahashi*

The Institute of Scientific and Industrial Research, Osaka University, Ibaraki,
Osaka 567, Japan

Abstract: Rhodium-catalyzed reaction of ethyl 2-phenylethynylbenzoate under water-gas shift reaction conditions results in the formation of a tetracyclic lactone, indeno[1,2-c]isocoumarin, as a major product which is derived from bond fission of the ester group and C-H bond activation of the phenyl group. © 1997 Elsevier Science Ltd.

Carbonylation reactions have long continued to attract much interest and have been widely applied to organic syntheses.[1] The carbonylation of unsaturated substrates such as alkenes and alkynes under water-gas shift reaction conditions often produces novel products by the catalysis of transition metal carbonyls such as $Fe(CO)_5$,[2] $Ru_3(CO)_{12}$,[3] $Rh_6(CO)_{16}$.[4] We have previously reported the rhodium-catalyzed carbonylation of acetylenes giving furan-2(5H)-ones under water-gas shift reaction conditions.[5] We have also shown that the carbonylation of acetylenes bearing functional groups such as amino[6] and formyl groups[7] adjacent to the carbon-carbon triple bond afforded cyclic products incorporated with such functional groups. Here we report a new type of cyclic carbonylation of acetylenes, that is, phenylethynylbenzoates having a neighboring ester group undergo simultaneous carbonylation of the acetylene, C-H bond activation of the phenyl group and C-O bond fission of the ester group.

In a typical experiment, a mixture of ethyl 2-phenylethynylbenzoate **1a** (3 mmol), $Rh_6(CO)_{16}$ (0.3 mol%), PPh_3 (6.0 mol%), Et_3N (1.2 ml), and H_2O (0.3 ml) in 1,4-dioxane (30 ml) was placed in a 100 ml stainless steel autoclave under 100 atm of initial carbon monoxide and stirred at 180 °C for 15 h. After usual work-up, separation by flash column chromatography on silica gel (hexane/AcOEt = 3/1) gave cyclic lactone **2**, indeno[1,2-c]isocoumarin, in 69% yield along with hydrogenated product **3a** in 28% yield [eqn. (1)].



(1)

1 (R = Et (**a**), Me (**b**), *i*-Pr (**c**) and Ph (**d**)) **2** **3**

The structure of **2** was characterized by ^1H and ^{13}C NMR, IR, and mass spectra,[8] and finally determined by X-ray crystallographic analysis.[9] The ORTEP drawing is illustrated in Figure 1, showing that the four rings in tetracyclic lactone **2** lie almost on the same plane.

Formation of **2** can be accounted for by elimination of the ethoxy group from and addition of one molecule each of carbon monoxide and hydrogen to the starting substrate **1a**. The elimination of the ethoxy group from **1a** was confirmed by observing the formation of ethanol after the reaction. An experiment employing D_2O instead of H_2O indicated that the hydrogen comes from water. Thus, the tetracyclic skeleton of **2** must be built up by the carbonylation of **1a** accompanied by C-O bond fission of the ester group and C-H bond activation of the phenyl group.

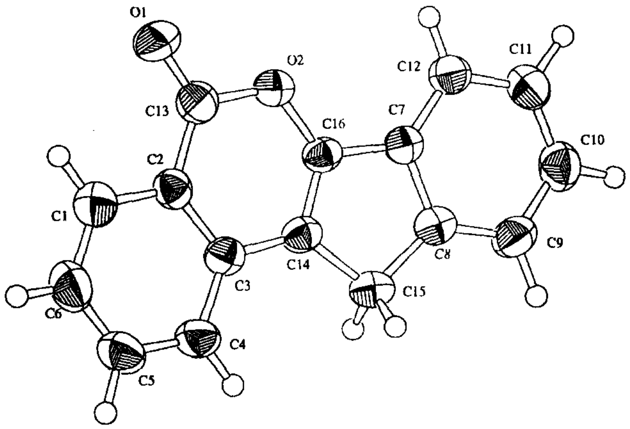


Figure 1. ORTEP drawing of **2**.

The yield of **2** is strongly influenced by reaction temperature (Table 1). The reaction at 80 °C afforded neither **2** nor **3**, but gave furanone derivatives, 3-(2'-ethoxycarbonyl)phenyl-4-phenylfuran-2(5H)-one (**4a**)[10] and 4-(2'-ethoxycarbonyl)phenyl-3-phenylfuran-2(5H)-one (**5a**),[10] in which the ester groups remain intact. The effective formation of **2** requires a higher reaction temperature than about 160 °C, preferably 180 °C. The addition of PPh_3 to the system lowered the catalytic activity, but resulted in considerable improvement in product selectivity because the formation of furanones was depressed.

Table 1. Rhodium-catalyzed cyclic carbonylation[a] of **1a**; Effect of reaction temperature and additive PPh_3

	Temp.	Time	Conv.	Yield[b](%)			
Entry	(°C)	(h)	(%)	**2**	**3a**	**4a**	**5a**
1[c]	180	15	100	69	28	-	-
2	180	15	100	45	18	15	12
3	80	10	100	-	-	59	39
4[c]	80	45	45	-	-	26	18

a) Reaction conditions: Substrate **1a**, 3 mmol; $Rh_6(CO)_{16}$, 0.3 mol%; CO, 100 atm; H_2O, 0.3 ml; NEt_3, 1.2 ml; 1,4-dioxane, 30 ml. b) Determined by HPLC. c) PPh_3 (6.0 mol%) was added to the reaction system.

Table 2 summarizes the results obtained from the cyclic carbonylation of several 2-phenylethynylbenzoates [eqn (1)]. Methyl 2-phenylethynylbenzoate gave **2** in 75% yield, but phenyl 2-phenylethynylbenzoate afforded **3** as a major product. Sterically larger substrates seem to give lower selectivity for **2**.

Table 2. Rhodium-catalyzed cyclic carbonylation[a] of **1**

	Substrate	Time	Yield[b](%)	
Entry	R	(h)	**2**	**3**
1	Et(**1a**)	15	69	28
2	Me(**1b**)	15	75	20
3	*i*-Pr(**1c**)	20	37	-[c]
4	Ph(**1d**)	20	18	68

a) Reaction conditions: Substrate **1a**, 3 mmol; $Rh_6(CO)_{16}$, 0.3 mol%; PPh_3, 6.0 mol%; CO, 100 atm; H_2O, 0.3 ml; NEt_3, 1.2 ml; Temperature 180 °C, 1,4-dioxane, 30 ml. b) Determined by HPLC. c) Complex mixture.

Although the reaction mechanism is not clear at present, it is obvious that three key steps are involved, that is, C-O bond fission of the ester group, C-H bond activation, and CO insertion. In separate experiments,[11] the reaction of **1a** at 80 °C for 10 h and then at 180 °C for 10 h did not afford tetracyclic lactone **2**, but only furanones **4a** and **5a** were formed as resulting products in a total yield of 80%, indicating that the present novel cyclic carbonylation proceeds *via* neither furanone **4** nor **5**. There are many examples of C (sp^2)-H activation in metal-catalyzed organic syntheses,[12] while very few C-O bond fissions of ester groups are known though Yamamoto and co-workers have shown C-O bond fission by the action of transition metal complexes on esters which leads to formation of (alkoxy)(acetyl)metal complexes.[13] It is noteworthy that such a tetracyclic ring system can be constructed directly from acetylenic substrates which are easily prepared by a palladium-catalyzed cross-coupling of aryl halides with terminal acetylenes.[14] Further studies are now in progress in order to extend the scope and establish the mechanism of the present novel reaction.

Acknowledgment. We are grateful to the Materials Analysis Center, ISIR, Osaka University for the support of spectral measurements and microanalyses.

References and notes

1. See, for example, Wender, I.; Pino, P. *Organic Syntheses via Metal Carbonyls*, John Wiley & Sons, New York, 1977, Vol. 2.
2. a) Reppe, W.; Vetter, H. *Ann.*, **1953**, *121*, 582; b) Kang, H. C.; Mauldin, C. H.; Cann, K.; Pettit, R. *J. Am. Chem. Soc.*, **1977**, *99*, 8323-8325; c) King, A. D.; King, D. B.; Yang, D. B. *J. Am. Chem. Soc.*, **1980**, *102*, 1028-1032.
3. a) Ungermann, C.; Landis, V.; Moya, S. A.; Walker, H.; Rinker, R. G.; Ford, P. C. *J. Am. Chem. Soc.*, **1979**, *101*, 5922-5929; b) Bricker, J. C.; Nagel, C. C.; Shore, S. G. *J. Am. Chem. Soc.*, **1982**, *104*, 1444-1445.

4. a) Laine, R. M. *J. Am. Chem. Soc.*, **1978**, *100*, 6451-6454; b) Chini, P.; Longoni, G.; Albano, V. *Adv. Organomet. Chem.*, **1976**, *14*, 285-344; c) Kaneda, K.; Hiraki, M.; Sano, K.; Imanaka, T.; Teranishi, S. J. *Mol. Catal.*, **1980**, *9*, 227-233.

5. Joh, T.; Doyama, K.; Onitsuka, K.; Shiohara, T.; Takahashi, S. *Organometallics*, **1991**, *10*, 2493-2497.

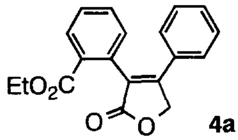
6. Hirao, K.; Morii, N.; Joh, T.; Takahashi, S. *Tetrahedron Lett.*, **1995**, *36*, 6243-6246.

7. Sugioka, T.; Zhang, S.-W.; Morii, N.; Joh, T.; Takahashi, S. *Chem. Lett.*, 1996, 249-250.

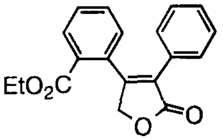
8. Data for indeno[1,2-c]isocoumarin: FT-IR(KBr) 1738 $cm^{-1}(\nu_{C=O})$; ^1H-NMR (400 MHz, $CDCl_3$) δ 8.09-8.17(m, 8H), 3.80(s, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 162.9, 154.0, 141.4, 136.3, 136.2, 135.1, 131.1, 127.6, 127.4, 127.3, 124.8, 122.3, 119.9, 119.0, 115.6, 31.9; Mass: m/z 234(M^+); mp 172-173 °C; Anal. calcd. for $C_{16}H_{10}O_2$: C 82.04, H 4.30%; Found: C 82.12, H 4.13%.

9. Crystal data for indeno[1,2-c]isocoumarin **2**: $C_{16}H_{10}O_2$, M = 234.25, crystal dimensions 0.70 x 0.50 x 0.40 mm, colorless, prismatic, monoclinic, space group $P2_1/c$(#14), a = 10.390(2), b = 15.036(2), c = 7.172(2) Å, $\beta = 91.12(2)°$, V = 1120.2(3) $Å^3$, Z = 4, *Dcalc* = 1.389 g/cm^3, μ(Mo-Kα) = 0.91 cm^{-1}, ω-2θ scan, $6.0 < 2\theta < 55.0°$, $R(R_w) = 0.058(0.048)$ for 203 parameters against 1540 reflections [$I > 3\sigma(I)$] out of 2689 unique reflections corrected for absorption using φ-scan technique and decay, GOF = 3.13. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1. Selected bond distances (Å) and angles (°): O(1)-C(13) 1.200(3), O(2)-C(13) 1.396(3), O(2)-C(16) 1.371(3), C(14)-C(16) 1.339(4), C(14)-C(15) 1.507(4); O(2)-C(13)-C(2) 117.2(3), C(13)-O(2)-C(16) 119.2(2), O(2)-C(16)-C(14) 124.8(3), C(3)-C(14)-C(16) 120.4(3), C(7)-C(16)-C(14) 112.9(3), C(15)-C(14)-C(16) 108.6(3).

10. The structures of furanones **4a** and **5a** are as follows:



4a



5a

11. Reaction conditions: Substrate **1a** (3 mmol), $Rh_6(CO)_{16}$ (0.3 mol%), PPh_3 (6.0 mol%), CO 100 atm, H_2O (0.3 ml), NEt_3 (1.2 ml), 1,4-dioxane (30 ml).

12. a) Mori Y.; Tsuji, J. *Tetrahedron*, **1972**, *28*, 29; b) Matsumoto, H.; Nakano, T.; Ohkawa, K.; Nagai, Y. *Chem. Lett.*, 1978, 363-366; c) Molander, G. A.; McKie, J. A. *J. Org. Chem.*, **1993**, *58*, 7216-7227.

13. a) Yamamoto, T.; Ishizu, J.; Kohara, T.; Komiya, S.; Yamamoto, A. *J. Am. Chem. Soc.*, **1980**, *102*, 3758-3764; b) Hayashi, Y.; Yamamoto, T.; Yamamoto, A.; Komiya, S.; Kushi, Y. *J. Am. Chem. Soc.*, 1986, *108*, 385-391; c) Yamamoto, T.; Miyashita, S.; Naito, Y.; Komiya, S.; Ito, T.; Yamamoto, A. *Organometallics*, **1982**, *1*, 808-812.

14. Takahashi, S.; Kuroyama, Y.; Sonogashira, K.; Hagihara, N. *Synthesis*, 1980, 627-630.

(*Received in Japan* 14 *April* 1997; *revised* 29 *May* 1997; *accepted* 30 *May* 1997)