Dimethyl (2Z,4Z)-3-(Dimethoxymethyl)-2,4-hexadienedioate (53). The ester **16** (300 mg) was partially converted to **53** and the product purified as described for the conversion of **37** into **51** to give, in the order of elution from the column, 100 mg (27%) of oily **53**, 40 mg of a mixture of **37** and **46**, and 150 mg of **16** (50% recovery). **53**: IR (film) 1720 (s), 1640 (m) cm^{-1}; UV (CH_3OH) λ_{max} 248 nm (ϵ 7900); ^1H NMR ($CDCl_3$) δ 3.46 (OCH_3), 3.72 and 3.75 ($COOCH_3$), 5.98 (s, CH), 5.99 (sharp d, H5), 6.26 (br s, H2), 6.73 (br d, H4) [$^3J_{4,5}$ = 12.5 Hz]; mass spectrum, *m/e* (relative intensity, fragment) 213 (4, M - OCH_3), 185 (20, M - $COOCH_3$), 75 [100, $CH(OCH_3)_2$].

Anal. Calcd for $C_{11}H_{16}O_6$: C, 54.09; H, 6.60. Found: C, 54.29; H, 6.71.

Alkaline hydrolysis of **53** (50 mg) carried out as described for **48** (see synthesis of **49**) gave a mixture of **41** and **45** in a ratio of 1:1 (^1H NMR). Acid-catalyzed hydrolysis of **53** (100 mg) carried out as described for **46** (see synthesis of **13**) gave a complex mixture containing **13** as a main product (^1H NMR), not further investigated.

(5R*,6S*)-2,8-Dioxo-6-methoxy-1,7-dioxaspiro[4.4]nonane (55). A flask containing **45** (50 mg) was immersed for 2 min in an oil bath heated to 200 °C, to give practically pure **55** as a thick oil: IR (film) 1800-1760 (s), 1600 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.65 and 3.09 (each d, CH_2, $^2J_{AB}$ = 17.5 Hz), 3.54 (OCH_3), 5.24 (CH), 6.27 and 7.49 (each d, respectively H3 and H4, $^3J_{3,4}$ = 6 Hz); mass spectrum, *m/e* (relative intensity, fragment) 184 (0.2, M), 153 (14, M - OCH_3), 124 (100, M - OCH_3 - HCO).

Anal. Calcd for $C_8H_8O_5$: C, 52.18; H, 4.38. Found: C, 52.47; H, 4.11.

Trimethyl (1Z,3E)-1,3-Butadiene-1,2,4-tricarboxylate (56). A mixture of 250 mg of **36**, 3 g of silver oxide, and 4 mL of methyl iodide in 25 mL of acetone was shaken overnight, filtered, and evaporated and the residue chromatographed on a 2 × 28 cm silica gel column, using benzene-ethyl acetate (4:1). Evaporation of appropriate fractions afforded 60 mg (18%) of the triester, eluted before 60 mg of **37**; the product was recrystallized from ether-petroleum ether: mp 51-52 °C; IR (KBr) 1755 (s), 1720 (s), 1630 (m), 1615 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.78 (2 $COOCH_3$), 3.91 ($COOCH_3$), 6.14 (d, H4), 6.17 (s, H1), 7.26 (d, H3) [$^3J_{3,4}$ = 16 Hz].

Anal. Calcd for $C_{10}H_{12}O_6$: C, 52.63; H, 5.30. Found: C, 52.80; H, 5.14.

Registry No. **1**, 119183-12-9; **2**, 81158-22-7; **3**, 119183-13-0; **5**, 119183-14-1; **6**, 119183-15-2; **7**, 119183-16-3; **8**, 119183-17-4; **9**, 119183-18-5; **10**, 119183-19-6; **11**, 119183-20-9; **12**, 119183-21-0; **13**, 119183-22-1; **14**, 119207-75-9; **15**, 119183-23-2; **16**, 119183-24-3; **17**, 119207-76-0; **18**, 81158-24-9; **19**, 119183-25-4; **23**, 119183-26-5; **24**, 81158-25-0; **25**, 119183-27-6; **26**, 119183-28-7; **29**, 119183-29-8; **30**, 81158-30-7; **31**, 119183-30-1; **32**, 119183-31-2; **33**, 119183-32-3; **36**, 119183-33-4; **37**, 119183-34-5; **38**, 119183-35-6; **39**, 119183-36-7; **40**, 119183-37-8; **41**, 119183-38-9; **42**, 119183-39-0; **43**, 119183-40-3; **44**, 119183-41-4; **45**, 119183-42-5; **46**, 119183-43-6; **47**, 119183-44-7; **48**, 119183-45-8; **49**, 119183-46-9; **50**, 119183-47-0; **51**, 119183-48-1; **53**, 119183-49-2; **55**, 119183-50-5; **56**, 119183-51-6.

Catalytic Synthesis of Vinyl Carbamates from Carbon Dioxide and Alkynes with Ruthenium Complexes

Roger Mahé,† Yoshiyuki Sasaki,‡ Christian Bruneau,† and Pierre H. Dixneuf*,†

Laboratoire de Chimie de Coordination Organique, URA CNRS D0415, Campus de Beaulieu, Université de Rennes, 35042 Rennes Cedex, France, and National Research Institute for Pollution and Resources, Agency of Industrial, Science and Technology, Onogawa 16-3, Tsukuba-shi, 305 Japan

Received October 4, 1988

Terminal alkynes react with carbon dioxide and secondary amines in the presence of ruthenium complexes to afford vinyl carbamates in one step. The reaction has been performed with phenylacetylene, hexyne, and acetylene and with dialkylamines, morpholine, piperidine, and pyrrolidine. Mononuclear ruthenium complexes such as $RuCl_2(PR_3)$(arene) and $RuCl_2$(norbornadiene)$(pyridine)_2$ for monosubstituted alkynes in the range 100-125 °C and [$RuCl_2$(norbornadiene)]$_n$ or even $RuCl_3 \cdot 3H_2O$ in the case of acetylene at 90 °C appear to be the best catalyst precursors. The addition of the carbamate takes place essentially at the terminal carbon of the alkyne and ruthenium-vinylidenes are suggested as catalytic active species to account for the observed regioselectivity.

Vinyl carbamates, or enol carbamates, have been shown to be useful intermediates for the access to agricultural chemicals, pharmaceutical product intermediates, or precursors of transparent polymers.[1] General methods leading to alkyl carbamates involving isocyanates or chloroformates, or using catalytic carbonylation processes of amines[2] or nitroarenes[3] in the presence of alcohols, are not suitable for the direct access to enol carbamates. These unsaturated carbamates have been previously prepared either by dehydrohalogenation of α-halogeno-[4] or β-halogenoalkyl carbamates[5] or by addition of amines to the vinyl chloroformates[6,7] resulting from dehydrohalogenation[8] or from enolmercury(II) derivatives.[6] The in situ generation of alkylidenecarbenes in the presence of isocyanates has also led to N-monosubstituted vinyl carbamates.[9] Each of these multistep syntheses of enol carbamates uses phosgene at one stage.

We have been looking for processes allowing the replacement of phosgene by carbon dioxide which, in con-

† Université de Rennes.
‡ National Research Institute for Pollution and Resources.

(1) (a) Boivin, S.; Chettouf, A.; Hemery, P.; Boileau, S. *Polym. Bull.* **1983**, *9*, 114. (b) Khur, R. J.; Dorough, H. W. *Carbamate Insecticides: Chemistry, Biochemistry and Toxicology*; CRC Press, Cleveland, OH, 1976.

(2) (a) Murahashi, S. I.; Mitsue, Y.; Ike, K. *J. Chem. Soc., Chem. Commun.* **1987**, 125. (b) Alper, H.; Vasapollo, G.; Hartstock, F. W.; Mlekuz, M. *Organometallics* **1987**, *6*, 2391. (c) Fukuoka, S.; Chono, M.; Kohno, M. *J. Chem. Soc., Chem. Commun.* **1984**, 399.

(3) Cenini, S.; Pizzotti, M.; Crotti, C.; Porta, F.; La Monica, G. *J. Chem. Soc., Chem. Commun.* **1984**, 1286.

(4) (a) Olofson, R. A.; Wooden, G. P.; Marks, J. T. Eur. Pat. 104984; *Chem. Abstr.* **1984**, *101*, 190657u. (b) Franco-Filipasic, B. R.; Patarcity, R. *Chem. Ind.* **1969**, *8*, 166.

(5) (a) Overberger, C. G.; Ringsdorf, H.; Weinshenker, N. *J. Org. Chem.* **1962**, *27*, 4331. (b) Shimizu, M.; Tanaka, E.; Yoshioka, H. *J. Chem. Soc., Chem. Commun.* **1987**, 136.

(6) Olofson, R. A.; Bauman, B. A.; Vancowicz, D. J. *J. Org. Chem.* **1978**, *43*, 752.

(7) Olofson, R. A.; Schnur, R. C.; Bunes, L.; Pepe, J. P. *Tetrahedron Lett.* **1977**, 1567. Olofson, R. A.; Schnur, R. C. *Ibid.* **1977**, 1571.

(8) Kung, F. E. U.S. Pat. 1945, 2377085. Lee, L. H. *J. Org. Chem.* **1965**, *30*, 3943.

0022-3263/89/1954-1518$01.50/0

Table I. Synthesis of Enol Carbamates Catalyzed by Polynuclear Ruthenium Complexes[a]

run	alkyne[a]	complex	solvent	t, °C	convsn,[b] %	total yield,[b] %	carbamate distribution, % 1A	2A	3A
1	a	$Ru_3(CO)_{12}$	toluene	125	92	17	35	65	0
2	a	$Ru_3(CO)_{12}$	CH_3CN	125	100	14	50	36	14
3	a	$Ru_3(CO)_{12}$	THF	125	91	17	35	65	0
4	a	$Ru_3(CO)_{12}$	CH_3CN	140	100	10	60	40	0
5	b	$Ru_3(CO)_{12}$	toluene	140	91	36	50	42	8
6	b	$Ru_3(CO)_{12}$	CH_3CN	140	91	18	61	33	6
7	b	$HRu_3(CO)_{11}^-,NEt_4^+$	THF	140	N.D.	34	50	41	9
8	b	$RuCo(CO)_7(\mu\text{-}PPh_2)$	CH_3CN	125	100	22	64	32	4

[a] Alkyne (10 mmol), diethylamine (20 mmol), solvent (10 mL), complex (0.2 mmol), CO_2 (5 MPa), reaction time 20 h, a = phenylacetylene, b = hex-1-yne. [b] Conversion and yields were determined by VPC and based on the initial alkyne.

trast, is not toxic but very stable. Although tremendous efforts have been made for the catalytic incorporation of CO_2 into organic substrates for their functionalization,[10] few efficient catalytic processes have been discovered.[10,11] It is known that amine and carbon dioxide are in equilibrium with ammonium carbamate,[12] which can thus be alkylated[13] and, on the other side, that ruthenium complexes can activate alkynes.[14] Thus, we have studied the possibility to activate alkynes toward the addition of ammonium carbamates. We now report that secondary amine, carbon dioxide, and *terminal* alkynes, in the presence of catalytic amount of a ruthenium complex, afford in *one-step* vinyl carbamates according to the following equation:

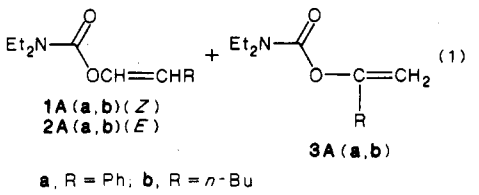
$$RC{\equiv}CH + CO_2 + HNR'_2 \longrightarrow RCH{=}CHOCNR'_2 \quad (O)$$

Preliminary results involving monosubstituted alkynes[15,16] and acetylene[17,18] have already been reported. The objectives of this paper are to give full details on the general reaction when optimized conditions were found and discuss selectivity and mechanism.

Results

Synthesis of Vinyl Carbamates with $Ru_3(CO)_{12}$. The activation of alkynes toward the addition of carboxylic acids has been shown to be performed by $Ru_3(CO)_{12}$ as catalyst precursor.[14] As ammonium carbamates, resulting from the addition of secondary amines to carbon dioxide, can be considered as a potential source of carbamic acids, we have examined the possibility of their addition to alkynes in the presence of $Ru_3(CO)_{12}$. Phenylacetylene (a) (10 mmol) was heated at 125–140 °C with an excess of carbon dioxide (5 MPa) and diethylamine (20 mmol) in 10 mL of solvent, such as toluene, tetrahydrofuran, or acetonitrile, and in the presence of $Ru_3(CO)_{12}$ (0.2 mmol). The formation of vinyl carbamates **1A(a)** (*Z* isomer), **2A(a)** (*E* isomer), and **3A(a)** was observed. Under similar conditions hex-1-yne (b) led to the formation of carbamates **1A(b)**, **2A(b)**, and **3A(b)** (eq 1, Table I).

$$Et_2NH + CO_2 + HC{\equiv}CR \xrightarrow{[Ru]} \underset{\mathbf{A}}{} \quad \underset{\mathbf{a,b}}{}$$



a, R = Ph; **b**, R = *n*-Bu

The reaction was regioselective. The addition of the carbamate took place mainly at the unsubstituted carbon atom of the alkyne leading to the *Z* (**1A**) and *E* (**2A**) isomers. The isomer **3A** was always obtained as a minor product.

The conversion of the alkyne was almost complete after 20 h, whereas the production of [(diethylcarbamoyl)oxy]hexene and [(diethylcarbamoyl)oxy]styrene did not exceed 36% and 17%, respectively (Table I). This indicated that the alkyne was partly involved in side reactions. From the reaction mixture, the *Z* and *E* isomers of 7-dodecen-5-yne and 1,4-diphenyl-3-buten-1-yne, the dimerization products of the alkyne were isolated and characterized; their overall yields varied in the range 10–30%, based on the initial alkyne. Some other polynuclear ruthenium complexes, $HRu_3(CO)_{11}^-$, NEt_4^+,[19] and $RuCo(CO)_7(\mu\text{-}PPh_2)$,[20] were tested and led to the same products with comparable yields in enol carbamates (Table I).

These first results showed that the catalytic activation of alkynes toward the addition of nucleophilic species, such as a carbamate anion, generated in situ from CO_2 and an amine, was possible in the presence of polynuclear ruthenium complexes. With these catalytic systems, dimerization and oligomerization of the alkyne were important, and thus the yield in vinyl carbamate moderate. Moreover, the involvement of bi- or polymetallic intermediate as catalytic active species might have been considered.[14] Thus, we investigated the behavior of mononuclear ruthenium complexes as catalyst precursors for the improvement of this synthesis and to gain insight in the nature of the active species.

Synthesis of Vinyl Carbamates with Mononuclear Ruthenium Complexes. (i) Addition of Secondary Amine and CO_2 to Phenylacetylene. Phenylacetylene

(9) Stang, P. J.; Anderson, G. H. *J. Org. Chem.* **1981**, *46*, 4585.
(10) (a) Inoue, S.; Yamazaki, N. *Organic and Bio-organic Chemistry of Carbon Dioxide*; Kodansha: Tokyo, 1982. (b) Aresta, A.; Forti, G. *Carbon Dioxide as a Source of Carbon*; Reidel: NATO ASI Series C, 1987, Vol. 206.
(11) Walther, D.; Schönberg, H.; Dinjus, E.; Sieler, J. S. *J. Organomet. Chem.* **1987**, *334*, 377.
(12) (a) Caplow, M. *J. Am. Chem. Soc.* **1968**, *2*, 1689. (b) Lallau, J. P.; Masson, J.; Guerin, H.; Roger, M. F. *Bull. Soc. Chim. Fr.* **1972**, *8*, 3111.
(13) Yoshida, Y.; Ishii, S.; Yamashita, T. *Chem. Lett.* **1984**, 1571.
(14) Rotem, M.; Shvo, Y. *Organometallics* **1983**, *2*, 1689.
(15) Sasaki, Y.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1986**, 790.
(16) Mahé, R.; Dixneuf, P. H.; Lécolier, S. *Tetrahedron Lett.* **1986**, 633.
(17) Sasaki, Y.; Dixneuf, P. H. *J. Org. Chem.* **1987**, *52*, 314.
(18) Bruneau, C.; Dixneuf, P. H.; Lécolier, S. *J. Mol. Catal.* **1988**, *44*, 175.
(19) Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Süss-Fink, G. *J. Chem. Soc., Dalton Trans.* **1979**, *9*, 1356.
(20) Regragui, R.; Dixneuf, P. H.; Taylor, N. J.; Carty, A. J. *Organometallics* **1984**, *3*, 1020.

Table II. Syntheses of Enol Carbamates Catalyzed by Mononuclear Ruthenium Complexes[a]

run	complex	t, °C	convsn,[b] %	carbamate yields,[b] %	carbamate distribution, % 1A(a)	2A(a)	3A(a)
9	$Ru(C_6Me_6)Cl_2PMe_3$	125	98	67	82	16	2
10	$Ru(NBD)(py)_2Cl_2$[c]	125	98	64	76	24	0
11	$Ru(p\text{-cymene})Cl_2PMe_3$	125	96	59	83	15	2
12	$Ru(p\text{-cymene})(CH_3CN)_2Cl^+,BF_4^-$	125	95	49	80	16	4
13	$RuCl_3{\cdot}3H_2O$	125	100	43	74	21	5
14	$Ru(p\text{-cymene})(py)_2Cl^+,BF_4^-$	125	76	35	80	20	0
15	$[Ru(p\text{-cymene})Cl_2]_2$	125	100	26	85	15	0
16	$Ru(p\text{-cymene})(PMe_3)_2Cl^+,PF_6^-$	125	96	18	67	22	11
17	$RuH_2(PPh_3)_4$	125	95	3	86	14	0
18	$RuCpCl(PPh_3)_2$[c]	125	36	1	100	0	0
19	$RuCl_3{\cdot}3H_2O$[d]	100	98	62	85	15	0
20	$Ru(\eta^6\text{-}C_6H_6)(\eta^4\text{-}C_6H_8)$[d]	100	54	32	84	16	0

[a] Phenylacetylene (10 mmol), diethylamine (20 mmol), CH_3CN (10 mL), complex (0.2 mmol), CO_2 (5 MPa), reaction time 20 h. [b] Conversion and yields were determined by VPC and based on the initial alkyne. [c] NBD = norbornadiene, py = pyridine, Cp = η^5-C_5H_5. [d] Solvent = THF (10 mL).

Table III. Catalytic Synthesis of Enol Carbamates. Influence of Solvent, Temperature, and CO_2 Initial Pressure[a]

run	solvent	t, °C	CO_2 pressure, MPa	convrsn,[b] %	carbamate yield,[b] %	carbamate distribution, % 1A(a)	2A(a)	3A(a)
21	CH_3CN	50	5	32	8	75	25	0
22	CH_3CN	125	5	98	64	77	23	0
23	toluene	100	5	98	50	80	18	2
24	toluene	140	5	100	47	79	17	4
25	THF	100	5	98	62	85	15	0
26	THF	100	2.5	94	62	85	15	0
27	THF	100	0.7	100	13	78	18	4
28	CH_3CN	100	5	100	70	80	20	0
29	hexane	100	5	95	49	86	14	0
30	MIBK[c]	100	5	82	48	81	19	0
31	acetone	100	5	87	45	80	20	0
32	decalin	100	5	100	24	79	20	1
33	dioxane	100	5	42	21	81	19	0
34	CH_2Cl_2	100	5	100	20	80	20	0
35	CH_3OH	100	5	87	3	67	33	0
36	toluene[d]	100	5	100	2	100	0	0

[a] Phenylacetylene (10 mmol), diethylamine (20 mmol), complex $RuCl_3{\cdot}3H_2O$ (0.2 mmol), reaction time 20 h. [b] Conversion and yield were determined by VPC and based on the initial alkyne. [c] MIBK = methyl isobutyl ketone. [d] Addition of PBu_3 (0.4 mmol).

was reacted with diethylamine and CO_2 at 100–125 °C in the presence of 0.02 equiv of a variety of mononuclear complexes. After 20 h, conversion of the alkyne was almost complete and vinyl carbamates **1A(a)** and **2A(a)** were produced in satisfactory yields (Table II). Most ruthenium(II) complexes appeared to be much more efficient catalysts than $Ru_3(CO)_{12}$, except the dihydride $RuH_2(PPh_3)_4$[21] and cyclopentadienyl–ruthenium $Ru(\eta^5\text{-}C_5H_5)Cl(PPh_3)_2$[22] complexes (runs 17 and 18), which exhibited no activity toward the carbamate formation. The best catalyst precursors were found in the series $RuX_2PR_3(\eta^6\text{-arene})$[23,24] (runs 9 and 11). $RuCl_2(pyridine)_2(norbornadiene)$[25] also had a high catalytic activity (run 10). Commercial hydrated ruthenium trichloride appeared to be a good precursor, especially at lower temperature (100 °C) (runs 13 and 19). Enol carbamates were also formed in the presence of a ruthenium(0) precursor, $[Ru(\eta^6\text{-}C_6H_6)(\eta^4\text{-}C_6H_8)]$[26] (run 20); however, this complex, which is easily oxidized, was probably transformed in the reaction mixture into ruthenium(II) species. A positive charge on the metal center had no significant effect on the catalytic activity, but substitution of chloride in a neutral complex by a basic phosphine led to a noticeable decrease of the yield in carbamates (runs 11 and 16).

The conversion of the alkyne was important and the *Z* and *E* isomers of 1,4-diphenyl-3-buten-1-yne, corresponding to the dimerization products of phenylacetylene, were also detected but in lower yields (<20%) than with $Ru_3(CO)_{12}$. The *Z* isomer **1A(a)** was always more abondant than the *E* isomer **2A(a)**, with approximately a *Z*/*E* ratio of 4. It is noteworthy that the formation of vinyl carbamates is highly regioselective with mononuclear complexes (Table II) as compared to $Ru_3(CO)_{12}$ (Table I). Better yields in carbamates **1A(a)** and **2A(a)** were obtained with mononuclear complex catalysts and only traces of **3A(a)** were detected, except in the case of $Ru(p\text{-cymene})(PMe_3)_2Cl^+,PF_6^-$ (run 16) for which an 11% yield of **3A(a)** was reached. Mononuclear ruthenium complexes strongly orientate the addition of the carbamate at the terminal carbon of the alkyne.

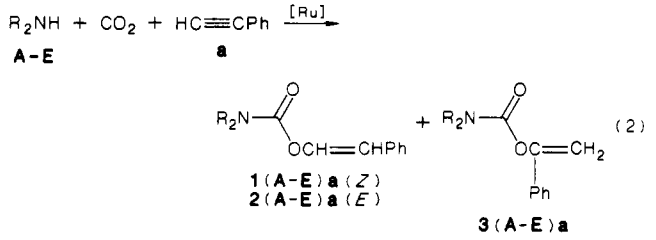
The influence of parameters on carbamate formation, such as time, temperature, solvents, and CO_2 pressure, was studied (Table III). Yields in carbamates were found to increase regularly up to 20 h of reaction time. The reaction was possible in a large range of temperature from 50 to 140 °C (runs 21–24), but the optimum was reached around 100 °C. At higher temperature, the formation of phenyl-

(21) Harris, R. O.; Hota, N. K.; Sadavoy, L.; Yuen, J. M. C. *J. Organomet. Chem.* **1973**, *54*, 259.
(22) Bruce, M. I.; Hameister, C.; Swinger, A. G.; Wallis, R. C. *Inorg. Synth.* **1982**, *21*, 79.
(23) Bennett, M. A.; Bruce, M. I.; Matheson, T. W. In *Comprehensive Organometallic Chemistry*; Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: 1982; Vol. 4, p 796.
(24) Le Bozec, H.; Touchard, D.; Dixneuf, P. H. *Adv. Organomet. Chem.*, in press.
(25) Potvin, C.; Manoli, J. M.; Pannetier, G.; Chevalier, R.; Platzer, N. *J. Organomet. Chem.* **1976**, *113*, 273.
(26) Pertici, P.; Vitulli, G. *Inorg. Synth.* **1983**, *22*, 176.

acetylene dimers and oligomers increased at the expense of the carbamate formation. The distribution of the *Z* and *E* isomers did not appear to be very sensitive to variation of the reaction temperature.

A wide variety of solvents was tested (runs 23, 25, and 28–35). Acetonitrile and tetrahydrofuran were found to be the most efficient, but the reaction was possible in many other solvents. Only alcohols and chlorinated solvents were not suitable. The addition of a free phosphine in the reaction mixture (run 36) inhibited the formation of enol carbamates and led to a quantitative production of the enynes (98%), resulting from dimerization of phenylacetylene. Thus, $RuCl_3 \cdot 3H_2O/2PBu_3$ could be an efficient catalyst system for the synthesis of enynes from terminal alkynes. The initial pressure of carbon dioxide was also an important factor (runs 25–27), a too low pressure leading to a decrease of the carbamate production and an increase of the formation of dimers.

The synthesis of vinyl carbamate derivatives from phenylacetylene and other secondary amines such as dimethylamine (B), piperidine (C), morpholine (D), and *N*-methyl-*N*-butylamine (E) has been attempted. Conditions analogous to that given in Table II were selected but using $RuCl_3 \cdot 3H_2O$ as catalyst precursor (0.2 mmol), with phenylacetylene (10 mmol), amine (20 mmol) in 10 mL of acetonitrile, or tetrahydrofuran and CO_2 (5 MPa). The corresponding β-styryl carbamates were produced on heating at 100 °C for 20 h (eq 2).



The reaction conditions were not optimized with amines B–E. The ratio of *Z*/*E* isomers (compounds **1** and **2**) was determined by ^1H NMR and VPC. The carbamates **1** and **2** were isolated by using chromatography from amines B (15%; **1**/**2** = 80/20), C (11%; **1**/**2** = 80/20), D (16%; **1** only), and E (5%, **1**/**2** = 65/35). For these amines B–E, the presence of the isomer **3** was not observed using VPC, pointing out the regioselectivity of the addition of the carbamate to the terminal carbon atom of the alkyne. The formation of carbamates **1** and **2** was accompanied by that of the dimerization products of phenylacetylene, which reached 22% yield with piperidine.

It is noteworthy that the catalytic formation of vinyl carbamates from terminal alkyne, CO_2, and amine is restricted to secondary alkylamines. No addition was observed with *N*-methylaniline, aniline, or primary amines such as isopropylamine, or *tert*-butylamine.

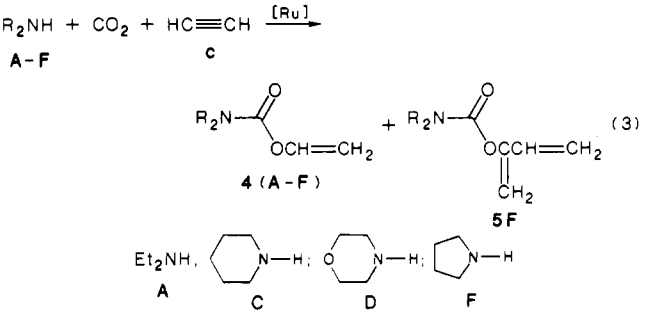
(ii) Synthesis of Vinyl Carbamates from Acetylene. Simple vinyl carbamates $CH_2{=}CHOCONR_2$ are useful monomers for the direct access to transparent polymers and varnish.[1a] The above results show that their formation by straightforward addition of ammonium carbamate to acetylene itself could thus be envisaged. However, few relevant examples of the use of the acetylene gas in catalysis have been reported, apart from the well-known nickel-catalyzed formation of acrylic derivatives by the Reppe process or Hg(II), Zn(II), and Cu(I) salts catalyzed addition of hydrochloric, acetic, and hydrocyanic acids to acetylene.

Table IV. Catalytic Synthesis of Vinyl Carbamates from Acetylene

run	complex	amine	*t*, °C	carbamate yield, %
37[a]	$RuCl_3 \cdot 3H_2O$	A	90	**4A** (10)
38[a]	$RuCl_3 \cdot 3H_2O$	D	90	**4D** (20)
39[b]	$[(NBD)RuCl_2]_n$	D	80	**4D** 36
40[a]	$RuCl_3 \cdot 3H_2O$	C	90	**4C** (34)
41[b]	$[(NBD)RuCl_2]_n$	C	90	**4C** 35
42[a]	$RuCl_3 \cdot 3H_2O$	F	90	**4F** (46)
43[b,c]	$[(NBD)RuCl_2]_n$	F	100	**4F** 63

[a] Acetylene (320 mmol), amine (100 mmol), complex (2 mmol), CH_3CN (50 mL), CO_2 (1.5 MPa), 20 h, isolated yields (%) based on the initial amine. [b] Acetylene (20 mmol), amine (7 mmol), ruthenium complex (0.2 mmol), CH_3CN (10 mL), CO_2 (2 MPa), 20 h, VPC yields based on the initial amine. [c] Complex (0.4 mmol) A = diethylamine, C = piperidine, D = morpholine, F = pyrrolidine.

We have searched for conditions allowing the addition to acetylene of ammonium carbamates. Acetylene (320 mmol) was introduced in an autoclave cooled at −50 °C and containing 50 mL of acetonitrile, 100 mmol of secondary amine, and 2 mmol of a mononuclear ruthenium complex. After introduction of CO_2 (1.5–2 MPa) the reaction mixture was heated at 80–100 °C for 20 h. Starting with diethylamine (A), piperidine (C), morpholine (D), and pyrrolidine (F), the corresponding vinyl carbamates **4** were produced in each case and isolated by distillation in 10 to 46% yields based on amine (eq 3, Table IV).



$Ru_3(CO)_{12}$[27] shows very low activity toward acetylene but ruthenium(II) derivatives including $[RuCl_2(\eta^6\text{-arene})]_2$ and $RuX_2PR_3(\eta^6\text{-arene})$ (X = Cl, I; PR_3 = PMe_3, PBu_3, PPh_3, PMe_2Ph) complexes[23,24] satisfactorily catalyzed addition of carbamates to acetylene. However, the best catalyst precursors were $RuCl_3 \cdot 3H_2O$ and $[RuCl_2(\text{norbornadiene})]_n$.[28] The optimum reaction conditions were very dependent on the nature of the amine and optimized conditions had to be determined for each amine (Table IV). Polymerization of acetylene into low and higher oligomers catalyzed by ruthenium precursors was noticed and a 3-fold excess of acetylene with respect to the amine was required. The addition of catalytic amounts of free phosphine inhibited the reaction, and the presence of maleic anhydride, which is known to promote reductive elimination on a metal center, had no effect.

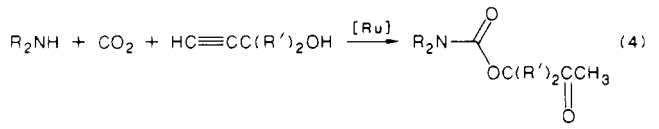
When pyrrolidine was used, besides the formation of **4F**, which was isolated in 46% yield, a byproduct was isolated in 2% yield and identified to be derivative **5F**. Compound **5F** corresponds actually to the addition of carbamic acid to 3-buten-1-yne, the dimerization product of acetylene

(27) Mantovani, A.; Cenini, S. *Inorg. Synth.* **1972**, *13*, 92.
(28) Abel, E. W.; Bennett, M. A.; Wilkinson, G. *J. Chem. Soc.* **1959**, 3178.

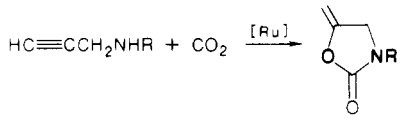
itself, which is formed during the reaction.

Discussion

Since our initial discovery of the addition of carbamates to ruthenium-activated terminal alkynes,[15,16] the addition of ammonium carbamates to functional alkynes has been carried out.[29-31] Thus, CO_2 and amines add to propargyl alcohols in the presence of ruthenium catalysts to give β-oxopropyl carbamates in good yields[29-31] (eq 4). Cyclic enol carbamates were obtained either by the reaction of propargyl alcohols with CO_2 and primary amine[29] or more generally by that of CO_2 with N-substituted propargylamines[31] (eq 5). 2-Hydroxyalkyl carbamates have been recently obtained directly by addition of CO_2 and amines to epoxides catalyzed by aluminum–porphyrin derivatives.[32]

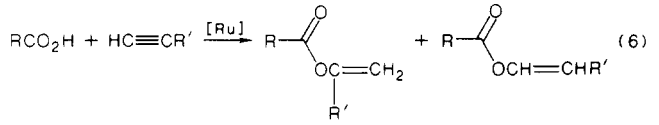


(4)



(5)

An important example of the activation of terminal alkynes by ruthenium catalysts has recently been shown by Mitsudo et al.[33] and us[34] for the addition of carboxylic acids, which leads to the regioselective synthesis of enol esters (eq 6). The best catalyst precursors for this synthesis appear to be, according to the nature of the acid, Ru(η^5-$C_8H_{11})_2$/PR_3/maleic anhydride,[33] $RuCl_3 \cdot xH_2O$/(alkyl)$_3$P,[33,34] or $RuCl_2(PR_3)$(arene)[34] systems.

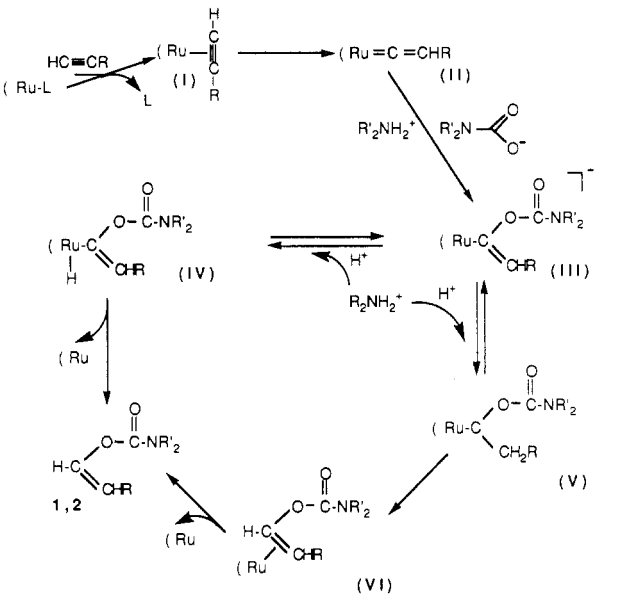


(6)

The addition of carboxylic acids to alkynes takes place with a high regioselectivity but the orientation is just opposite to that observed for the addition of carbamates to the same alkynes leading to compounds **1** and **2**. The vinyl carbamate formation clearly involves the addition of the carbamate anion to an active alkyne–ruthenium species. We have shown that the ruthenium-catalyzed addition of carbamates occurs only with terminal alkynes. The selective addition at the terminal alkyne carbon strongly suggests the formation of a ruthenium–vinylidene active species and thus a catalytic cycle as indicated in Scheme I.

Many examples are known of the rearrangement of (η^2-terminal alkyne)metal complexes of type I into (η^1-vinylidene)metal derivatives of type II, which display electrophilic behavior of the carbon atom bonded to the metal center.[35] Thus, the carbamate may add to the

Scheme I



electrophilic carbon of this vinylidene–ruthenium moiety, giving the intermediate III. Protonation at the metal by the ammonium cation, followed by classical reductive elimination from IV, is expected to lead to the enol carbamates **1** and **2**. An alternative route may consist in the protonation of species III at the basic β carbon atom, followed by a hydrogen-atom 1–2 shift in V, giving moiety VI, which on decoordination should afford compounds **1** and **2**. Indeed, such a hydrogen-atom 1–2 shift has been observed by Brookhart et al.[36] with isoelectronic iron carbene complexes.

Moreover, such a vinylidene–ruthenium intermediate was shown to be produced from one of the best catalysts, the (η^6-C_6Me_6)$RuCl_2PR_3$ complexes, and terminal alkynes,[37] they are very reactive and afford in the presence of methanol at room temperature (alkoxy)alkylcarbene–ruthenium complexes via classical addition of methanol.

Although the ruthenium–vinylidene mechanism cannot be proved, the catalytic formation of vinyl carbamates from terminal alkynes, CO_2, and secondary amines reported here is a novel use of terminal alkynes in synthesis, an unprecedented example of catalytic reaction involving CO_2, and a new general synthesis of vinyl carbamates that is not based at one stage on the use of phosgene. This reaction offers a potential for both the activation of alkynes by ruthenium and the possibility of incorporation of carbamates or CO_2 adducts to organic substrates.

Experimental Section

Proton NMR spectra were recorded on JEOL MH 100 or Brucker AM 300 WB nuclear magnetic spectrometers respectively at 100 and 300 MHz. Infrared spectra were recorded on a Pye Unicam SP 1100 spectrometer. VPC analyses were obtained with an Intersmat IGC 120 FLD chromatograph equipped with a flame ionization detector; 1.5 m × 2.1 mm stainless steel columns packed with 10% FFAP or 15% Apiezon L on Chromosorb WHMDS (80/100 mesh) were used.

Secondary amines, acetylenic compounds, and carbon dioxide were commercially available. All solvents were distilled over drying materials under an inert atmosphere prior to use. Ruthenium complexes were prepared from $RuCl_3 \cdot 3H_2O$ according to reported

(29) Sasaki, Y.; Dixneuf, P. H. *J. Org. Chem.* **1987**, *52*, 4389.
(30) Bruneau, C.; Dixneuf, P. H. *Tetrahedron Lett.* **1987**, *28*, 2005.
(31) Mitsudo, T.; Hori, Y.; Yamakawa, Y.; Watanabe, Y. *Tetrahedron Lett.* **1987**, *28*, 4417.
(32) Kojima, F.; Aida, T.; Inoue, S. *J. Am. Chem. Soc.* **1986**, *108*, 391.
(33) (a) Mitsudo, T.; Hori, Y.; Yamakawa, Y.; Watanabe, Y. *Tetrahedron Lett.* **1986**, *27*, 2125; (b) *J. Org. Chem.* **1987**, *52*, 2230.
(34) (a) Ruppin, C.; Dixneuf, P. H. *Tetrahedron Lett.* **1986**, *27*, 6323. (b) Ruppin, C.; Dixneuf, P. H.; Lecolier, S. *Tetrahedron Lett.* **1988**, *29*, 5365.
(35) (a) Bruce, M. I.; Swincer, A. G. *Adv. Organomet. Chem.* **1983**, *22*, 59. (b) Silvestre, J.; Hoffman, R. *Helv. Chim. Acta* **1985**, *68*, 1461.
(36) Brookhart, M. S.; Tucker, J. R.; Husk, G. R. *J. Am. Chem. Soc.* **1983**, *105*, 258.
(37) Ouzzine, K.; Le Bozec, H.; Dixneuf, P. H. *J. Organomet. Chem.* **1986**, *317*, 25.

methods: $RuX_2PR_3(\eta^6$-arene), ref 23; $(RuCl_2$(norbornadiene))$_n$, ref 27; $RuCl_2$(pyridine)$_2$(norbornadiene), ref 25; $RuH_2(PPh_3)_4$, ref 21; $Ru(\eta^5$-$C_5H_5)Cl(PPh_3)_2$, ref 22; $[Ru(\eta^6$-$C_6H_6)(\eta^4$-$C_6H_8)]$, ref 26; $Ru_3(CO)_{12}$, ref 28; $HRu_3(CO)_{11}NEt_4$, ref 19; and $RuCo(CO)_7(\mu$-$PPh_2)$, ref 20.

Addition to Terminal Alkynes. In a typical run, solvent (10 mL), secondary amine (20 mmol), alkyne (10 mmol), and ruthenium complex (0.2 mmol) were placed in a 125-mL stainless steel autoclave. Carbon dioxide was used first to flush out the reactor and then to pressurize it to the starting pressure (5 MPa). The reaction mixture was stirred at 100–140 °C for 20 h. After cooling, the autoclave was washed with solvent and the solution concentrated to about 10 mL. The enol carbamates were analyzed by VPC using hexamethylbenzene or triphenylmethane as internal standard. After elimination of the solvent, organic compounds (carbamates and enynes) were collected under reduced pressure. Thick layer chromatography of these products with a dichloromethane–petroleum ether mixture (1/1) as eluent gave a good separation of the enol carbamates from the enynes.

(*Z*)-β-[(Diethylcarbamoyl)oxy]styrene (1A(a)): ^{1}H NMR (C_6D_6, 300 MHz) δ 7.56 (d, 1, J = 7.5 Hz, =CHO), 7.4 (m, 5, Ph), 5.44 (d, 1, J = 7.5 Hz, =CHPh), 3.06 (q, 2, J = 7 Hz, NCH_2), 2.95 (q, 2, J = 7 Hz, NCH_2), 0.90 (t, 3, J = 7 Hz, CH_3), 0.84 (t, 3, J = 7 Hz, CH_3); IR (neat) ν 1730 (C=O), 1660 (C=C) cm^{-1}; MS m/z 219.126 (M^+).

(*E*)-β-[(Diethylcarbamoyl)oxy]styrene (2A(a)): ^{1}H NMR (C_6D_6, 300 MHz) δ 8.16 (d, 1, J = 12.9 Hz, =CHO), 7.4 (m, 5, Ph), 6.27 (d, 1, J = 12.9 Hz, =CHPh), 3.06 (q, 2, J = 7 Hz, NCH_2), 2.95 (q, 2, J = 7 Hz, NCH_2), 0.90 (t, 3, J = 7 Hz, CH_3), 0.84 (t, 3, J = 7 Hz, CH_3); IR (neat) ν 1730 (C=O), 1660 (C=C) cm^{-1}; MS m/z 219.126 (M^+).

(*Z*)-1-[(Diethylcarbamoyl)oxy]hex-1-ene (1A(b)): ^{1}H NMR (C_6D_6, 100 MHz) δ 6.96 (d, 1, J = 6 Hz, =CHO), 4.74 (dt, 1, $J_{CH=CH}$ = 6 Hz, J_{CH_2-CH} = 6 Hz, $CHCH_2$), 3.33 (q, 2, J = 7 Hz, NCH_2, 2.13 (m, 2, CH_2), 1.38 (m, 4, CH_2), 1.18 (t, 6, J = 7 Hz, CH_3CH_2N), 0.90 (t, 3, J = 6 Hz, $CH_3(CH_2)_3$); IR (neat) ν 1720 (C=O), 1670 (C=C) cm^{-1}; MS m/z 199.157 (M^+).

(*E*)-1-[(Diethylcarbamoyl)oxy]hex-1-ene (2A(b)): ^{1}H NMR (C_6D_6, 100 MHz) δ 6.92 (d, 1, J = 14 Hz, =CHO), 5.22 (dt, 1, $J_{CH=CH}$ = 14 Hz, J_{CH_2-CH} = 7 Hz, $=CHCH_2$), 3.30 (q, 4, J = 6 Hz, NCH_2), 1.34 (m, 2, CH_2), 1.20 (m, 4, CH_2), 1.14 (t, 6, J = 6 Hz, CH_3CH_2N), 0.88 (t, 3, J = 6 Hz, $CH_3(CH_2)_3$); IR (neat) ν 1720 (C=O), 1675 (C=C) cm^{-1}; MS m/z 199.157 (M^+).

(*Z*)-β-[(Dimethylcarbamoyl)oxy]styrene (1B(a)): ^{1}H NMR ($CDCl_3$, 100 MHz) δ 7.47 (d, 1, J = 8 Hz, =CHO), 7.2–7.35 (m, 5, Ph), 5.55 (d, 1, J = 8 Hz, =CHPh), 3.07 (s, 3, CH_3), 3.00 (s, 3, CH_3); IR (neat) ν 1730 (C=O), 1665 (C=C) cm^{-1}; MS m/z 191.095 (M^+).

(*E*)-β-[(Dimethylcarbamoyl)oxy]styrene (2B(a)): ^{1}H NMR ($CDCl_3$, 100 MHz) δ 7.72 (d, 1, J = 13 Hz, =CHO), 7.20–7.35 (m, 5, Ph), 6.24 (d, 1, J = 13 Hz, =CHPh), 3.07 (s, 3, CH_3), 3.00 (s, 3, CH_3); IR (neat) ν 1730 (C=O), 1665 (C=C) cm^{-1}; MS m/z 191.095 (M^+).

(*Z*)-β-[(Piperidinocarbamoyl)oxy]styrene (1C(a)): ^{1}H NMR ($CDCl_3$, 100 MHz) δ 7.15–7.25 (m, 5, Ph), 7.15 (d, 1, J = 9 Hz, =CHO), 5.48 (d, 1, J = 9 Hz, =CHPh), 3.51 (m, 4, CH_2N), 1.51 (m, 6, CH_2); IR (neat) ν 1725 (C=O), 1660 (C=C) cm^{-1}; MS m/z 231.126 (M^+).

(*Z*)-β-[(Morpholinocarbamoyl)oxy]styrene (1D(a)): ^{1}H NMR ($CDCl_3$, 100 MHz) δ 7.2 (m, 5, Ph, =CHO masked), 5.55 (d, 1, J = 8 Hz, =CHPh), 3.62 (m, 4, OCH_2), 1.24 (m, 4, NCH_2); IR (neat) ν 1725 (C=O), 1660 (C=C) cm^{-1}; MS m/z 233.105 (M^+).

(*Z*)-β-[(Methylbutylcarbamoyl)oxy]styrene (1E(a)): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.0–7.6 (m, 5, Ph), 7.6 (d, 1, J = 7 Hz, =CHO), 5.44 (d, 1, J = 7 Hz, =CHPh), 3.05 (t, 2, J = 7 Hz, NCH_2), 2.49 (s, 3, NCH_3), 1.30 (m, 4, CH_2), 0.79 (t, 3, J = 7 Hz, CH_3); IR (neat) ν 1725 (C=O), 1665 (C=C) cm^{-1}; MS m/z 233.141 (M^+).

(*E*)-β-[(Methylbutylcarbamoyl)oxy]styrene (2E(a)): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.20 (d, 1, J = 13 Hz, =CHO), 7.0–7.6 (m, 5, Ph), 6.31 (d, 1, J = 13 Hz, =CHPh), 2.89 (t, 2, J = 7 Hz, NCH_2), 2.49 (s, 3, CH_3N), 1.3 (m, 4, CH_2), 0.73 (t, 3, J = 7 Hz, CH_3); IR (neat) ν 1720 (C=O), 1660 (C=C) cm^{-1}; MS m/z 233.141 (M^+).

Addition to Acetylene. Secondary amine (100 mmol), ruthenium complex (2 mmol), and acetonitrile (50 mL) were first placed in the autoclave. Acetylene (320 mmol) was dissolved in the solvent under atmospheric pressure after cooling the autoclave to −50 °C. An excess of acetylene in the ratio acetylene/amine of about 3 was necessary. The reactor was then stirred under CO_2 pressure (1.5–2 MPa) at 80–100 °C for 20 h. The analysis of the reaction mixture was similar to that described above in the case of terminal alkynes.

[(Diethylcarbamoyl)oxy]ethylene (4A): ^{1}H NMR ($CDCl_3$, 100 MHz) δ 7.2 (dd, 1, J_{cis} = 6.5 Hz, J_{trans} = 15 Hz, =CHO), 4.70 (d, 1, J_{trans} = 15 Hz, $=CH_2$), 4.40 (d, 1, J_{cis} = 6.5 Hz, $=CH_2$), 3.3 (q, 4, J = 7 Hz, NCH_2), 1.1 (t, 6, J = 7 Hz, CH_3); IR (neat) ν 1720 (C=O), 1650 (C=C) cm^{-1}.

[(Piperidinocarbamoyl)oxy]ethylene (4C): ^{1}H NMR ($CDCl_3$, 100 MHz) δ 7.27 (dd, 1, J_{cis} = 6.5 Hz, J_{trans} = 15 Hz, =CHO), 4.76 (d, 1, J_{trans} = 15 Hz, $=CH_2$), 4.44 (d, 1, J_{cis} = 6.5 Hz, $=CH_2$), 3.47 (m, 4, CH_2N), 1.60 (m, 6, CH_2); IR (neat) ν 1715 (C=O), 1650 (C=C) cm^{-1}.

[(Morpholinocarbamoyl)oxy]ethylene (4D): ^{1}H NMR (CCl_4, 100 MHz) δ 7.21 (dd, 1, J_{cis} = 6.5 Hz, J_{trans} = 15 Hz, =CHO), 4.72 (d, 1, J_{trans} = 15 Hz, $=CH_2$), 4.42 (d, 1, J_{cis} = 6.5 Hz, $=CH_2$), 3.55 (m, 8, CH_2); IR (neat) ν 1720 (C=O), 1640 (C=C) cm^{-1}.

[(Pyrrolidinocarbamoyl)oxy]ethylene (4F): ^{1}H NMR ($CDCl_3$, 100 MHz) δ 7.20 (dd, 1, J_{cis} = 6 Hz, J_{trans} = 14 Hz, =CHO), 4.70 (d, 1, J_{trans} = 14 Hz, $=CH_2$), 4.33 (d, 1, J_{cis} = 6 Hz, $=CH_2$), 3.37 (m, 4, CH_2N), 1.80 (m, 4, CH_2); IR (neat) ν 1720 (C=O), 1640 (C=C) cm^{-1}.

Acknowledgment. We are grateful to the C.N.R.S.-S.N.P.E. "Groupement Scientifique CO_2" for financial support and to Dr. S. Lécolier for stimulating discussions.

Transition Metal Catalyzed Grignard Cross-Coupling to Ortho-Halogenated Aryl Imines. An Efficient Synthesis of Ortho-Substituted Aryl Aldehydes

Lendon N. Pridgen,* L. Snyder,[1a] and J. Prol, Jr.[1b]

Division of Chemical Research & Development, Smith Kline & French Laboratories, P.O. Box 1539, King of Prussia, Pennsylvania 19406-0939

Received November 17, 1988

N-(*o*-Halogenated benzylidene)cyclohexylamines **2** were successfully reacted with reducing and nonreducing Grignard reagents in a transition metal catalyzed cross-coupling reaction resulting in an efficient single-step synthesis of ortho-substituted benzaldehydes after acidic workup. The dihalogenated benzylidene amines reacted regioselectively at the imine-activated ortho position to yield ortho-substituted halogenated benzaldehydes.

Although various synthesis of aromatic aldehydes have been reported,[2] none filled our particular requirements for an efficient synthesis of an ortho-substituted benzaldehyde intermediate in the synthesis of a pharmacologically active

0022-3263/89/1954-1523$01.50/0