83999-74-0; **42c**, 84026-53-9; **42t**, 74924-35-9; **43c**, 2934-63-6; **43t**, 847-86-9; **46c**, 81012-16-0; **46t**, 81064-05-3; **47t**, 83999-53-5; **48c**, 83999-49-9; **48t**, 83999-76-2; **49t**, 81012-14-8; **50c**, 83999-55-7; **50t**, 81012-15-9; **56c**, 84009-47-2; **56t**, 84009-49-4; codeine, 76-57-3.

Supplementary Material Available: Tables of bond distances, bond angles, thermal parameters, and atom coordinates (6 pages). Ordering information is given on any current masthead page.

Rhodium Carbonyl Catalyzed Carbonylation of Unsaturated Compounds. 2.[1] Synthesis of 5-Alkoxy-2(5*H*)-furanones by the Carbonylation of Acetylenes in Alcohol[2]

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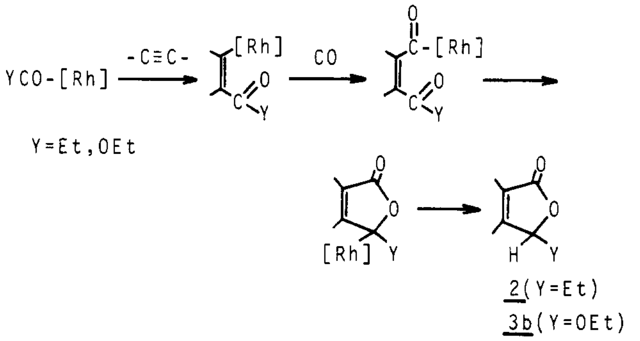
The carbonylation of diphenylacetylene (**1a**) in ethanol in the presence of $Rh_4(CO)_{12}/Na_2CO_3$ as a catalyst gave 5-ethoxy-3,4-diphenyl-2(5*H*)-furanone (**3b**) in a 72% yield, together with 3-(ethoxycarbonyl)-2-phenylindanone (11%) and diethyl 2,3-diphenylsuccinate (4%). The combination of rhodium catalysts with various bases was examined, and the $Rh_4(CO)_{12}$/NaOAc system was found to be the most suitable catalytic system (**3b**, 87% yield). The carbonylation of **1a** in various alcohols such as methanol, 1-propanol, 2-propanol, and 1-octanol gave 5-alkoxy-3,4-diphenyl-2(5*H*)-furanones in good yields. Disubstituted acetylenes such as a 1-phenylpropyne, 2-butyne, and 3-hexyne could be also used to give the corresponding furanones.

The carbonylation of acetylenes with carbon monoxide in the presence of a soluble transition-metal catalyst, particularly of group 8, is a useful synthetic reaction because it yields various valuable products according to the reaction conditions.[3,4] Carbonylation with ring closure presents a convenient route for the one-step synthesis of five- and seven-membered unsaturated lactones.[5,6] In the previous paper we have reported that the rhodium carbonyl catalyzed cross-hydrocarbonylation of acetylenes and ethylene in ethanol yields 5-ethyl-2(5*H*)-furanones (**2**), together with a small amount of 5-ethoxy-2(5*H*)-furanone (**3**).[1] It should be noted that the ethanol, used as the solvent, acts as a hydrogen donor in the formation of **2** and itself constitutes a part of the molecule in the formation of **3**.

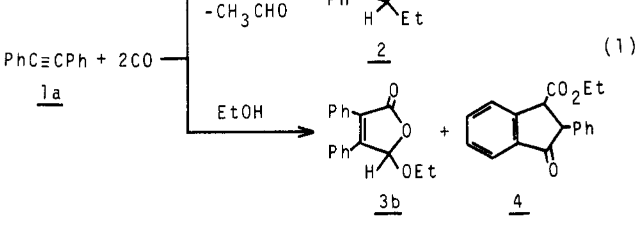
Although the carbonylation of acetylenes in alcohol has been known to give mono- and dicarboxylates such as acrylates, fumarates, maleates, and succinates, no report has appeared on the formation of 5-alkoxy-2(5*H*)-furanone (**3**). Since the furanone **3** is a new type of the carbonylation product from acetylene and is a member of an important class of naturally occuring butenolides,[7] its selective synthesis is desirable. We have found that addition of basic alkali metal salts to $Rh_4(CO)_{12}$ or its precursors improved remarkably the yield of **3**. Full details are described here of this new and facile method for the preparation of 5-alkoxy-2(5*H*)-furanone (**3**) from acetylenes, carbon monoxide, and alcohols.

Scheme I



Results and Discussion

As previously reported,[1] when a mixture of diphenylacetylene (**1a**) and a catalytic amount of $Rh_4(CO)_{12}$ in ethanol was heated at 125 °C under the pressure of C_2H_4 (20 kg/cm^2) and CO (30 kg/cm^2), 5-ethoxy-3,4-diphenyl-2(5*H*)-furanone (**3b**) and 3-(ethoxycarbonyl)-2-phenylindanone (**4**) were obtained in 4% and 11% yields, respectively, along with 5-ethyl-3,4-diphenyl-2(5*H*)-furanone (**2**, 31%; eq 1). The structure of **3b** was determined on the basis of its analytical and spectroscopic data. The IR



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[1] For part 1, see: (a) Hong, P.; Mise, T.; Yamazaki, H. *Nippon Kagaku Kaishi* **1982**, 242. (b) Hong, P.; Mise, T.; Yamazaki, H. *Chem. Lett.* **1981**, 989.

[2] A part of this work has been published as a preliminary report: Mise, T.; Hong, P.; Yamazaki, H. *Chem. Lett.* **1981**, 993.

[3] Pino, P.; Braca, G. "Organic Syntheses via Metal Carbonyls"; Wender, I., Pino, P., Eds.; Wiley: New York, 1977; Vol. 2, p 419.

[4] Mullen, A. "New Syntheses with Carbon Monoxide"; Falbe, J., Ed.; Springer-Verlag: West Berlin, 1980; p 414.

[5] (a) Sauer, J. S.; Cramer, R. D.; Engelhardt, V. A.; Ford, T. A.; Holmquist, H. E.; Houk, B. W. *J. Am. Chem. Soc.* **1959**, *81*, 3677. (b) Albanesi, G.; Tovaglieri, M. *Chim. Ind. (Milan)* **1959**, *41*, 189. (c) Tsuji, J.; Nogi, T. *J. Am. Chem. Soc.* **1966**, *88*, 1289.

[6] Foa, M.; Cassar, L.; Tacchiventri, M. *Tetrahedron Lett.* **1968**, 1357.

[7] Rao, Y. S. *Chem. Rev.* **1976**, *76*, 625.

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Table I. Influence of Various Bases in the Carbonylation of **1a** with Ethanol[a]

base	product yield,[b] % **3b**	**5**	**4**
none	5	2	22
NaOEt	6	3	0
NaOH	8	2	3
$NaHCO_3$	37	8	0
Na_2CO_3	41	10	0
NaOAc	78	11	4
Li_2CO_3	61	6	22
K_2CO_3	11	3	0
Rb_2CO_3	14	2	0
Cs_2CO_3	16	0	0
$CaCO_3$	4	2	22
$BaCO_3$	3	3	18
LiOAc	62	13	3
KOAc	59	15	3
RbOAc	47	11	0
CsOAc	58	12	0

[a] Operating conditions: **1a**, 1.0 mmol; $Rh_4(CO)_{12}$, 0.025 mmol; base, 1.0 mmol; CO, 40 kg/cm^2; EtOH, 15 mL; 125 °C, 6 h. [b] Determined by GC.

Table II. Carbonylation of **1a** with Ethanol under Various Conditions[a]

P_{CO}, kg/cm^2	temp, °C	product yield,[b] % **3b**	**5**	**4**	recovery of **1a**,[b] %
40	125	78	11	4	0
40	75	76	7	3	4
40	50	47	6	0	32
40	30	9	1	0	70
20	75	53	5	0	29
10	75	45	5	0	33

[a] Operating conditions: **1a**, 1.0 mmol; $Rh_4(CO)_{12}$, 0.025 mmol; NaOAc, 1.0 mmol; EtOH, 15 mL; 6 h. [b] Determined by GC.

Table III. Carbonylation of **1a** with Ethanol in the Presence of Rhodium Compounds and Sodium Salts[a]

catalyst	temp, °C	product yield,[b] % **3b**	**5**	**4**	recovery of **1a**,[b] %
$Rh_4(CO)_{12}$/NaOAc	125	87	8	4	0
$Rh_4(CO)_{12}/Na_2CO_3$	125	72	4	11	3
$RhCl_3/Na_2CO_3$[c]	100	54	6	7	16
	125	68	7	14	2
	150	42	14	8	0
	180	0	0	0	79
$RhCl_3$/NaOAc[c]	125	75	11	4	1
Rh_2O_3/NaOAc	125	75	10	5	0
$RhCl(PPh_3)_3$/NaOAc	125	10	1	0	23

[a] Operating condition: **1a**, 10 mmol; catalyst, 0.1 mmol; base, 1.0 mmol; EtOH, 50 mL; 6 h. [b] Determined by GC. [c] Base, 10 mmol.

spectrum of **3b** showed bands at 1760 ($\nu_{C=O}$) and 1655 cm^{-1} ($\nu_{C=C}$) similar to those of **2** (1732 and 1642 cm^{-1}), and the ^{1}H NMR spectrum showed signals at δ 1.28 (t, Me), 3.6–4.2(m, OCH_2), 6.20 (s, OCHO), and 7.4 (m, 2 Ph).

The formation of **3b** and **4** is competitive with the formation of **2** from a common catalyst molecule, from which acylrhodium and (ethoxycarbonyl)rhodium species may be generated as the key intermediates for formation of **2**[1] and for **3b**, respectively, as shown in Scheme I. Thus suppression of the formation of **2** may increase the yields of **3b** and **4**. The reaction was executed without ethylene. But, the yields of **3b** and **4** were increased only to 11% and 27%, respectively. The low yield of **3b** even in the absence of ethylene may be due to slow generation of the (ethoxycarbonyl)rhodium intermediate from ethanol compared with the facile formation of the acyl analogue from ethylene.

It is known that an (ethoxycarbonyl)rhodium cluster anion, $[Rh_6(CO)_{15}(CO_2Et)]^-$, is formed by the reaction of $Rh_4(CO)_{12}$ or $Rh_2(CO)_4Cl_2$ with ethanol in the presence of Na_2CO_3.[8a] We examined the addition of Na_2CO_3 or related basic reagents to the rhodium catalyst and found that the yield of **3b** became remarkably higher by adding some basic alkali metal salts. Thus, when a mixture of **1a** (10 mmol), $Rh_4(CO)_{12}$ (0.025 mmol), and Na_2CO_3 (1.0 mmol) in ethanol (50 mL) was heated at 125 °C under the pressure of CO (50 kg/cm^2), **3b** was obtained in a 72% yield, accompanied by **4** (11%) and diethyl 2,3-diphenylsuccinate (**5**,[9] 4%).

In order to find a more suitable system and to clarify the role of added base, we examined various bases under the reaction conditions of a base (1.0 mmol), **1a** (1.0 mmol), and $Rh_4(CO)_{12}$ (0.025 mmol) in ethanol (15 mL). The results are shown in Table I. Among bases examined, sodium acetate (NaOAc) gave the highest yield of **3b**. Reasonable results were also obtained by using milder bases (Na_2CO_3 and $NaHCO_3$). But, addition of stronger bases (NaOH and NaOEt) gave no effect. These observations are consistent with the stability of $Na[Rh_6(CO)_{15}(COOR)]$ under basic conditions.[8b] In comparison with Li_2CO_3 and Na_2CO_3, carbonates of K, Rb, and Cs showed low effectiveness, and those of alkaline earth metals gave no effect. Within the alkali metal acetates no distinct differences were observed.

The succinate **5** was confirmed to be a secondary product derived by alcoholysis of **3b**; the mixture of **3b** and excess Na_2CO_3 in ethanol was heated at 150 °C to give **5b** in a 70% yield. By use of sodium and lithium carbonates or alkali metal acetates, the amounts of the product **5** reached about 20% of those of **3b**. This seems to be due to a relatively high concentration of the added base. On the other hand, the added base did not contribute to the formation of the indanone **4**.

Using the optimized $Rh_4(CO)_{12}$/NaOAc system, we varied the other reaction conditions. The results summarized in Table II show that the reaction can proceed even under relatively mild conditions such as under a 10-kg/cm^2 pressure and at 75 °C.

Rhodium catalysts such as Rh_2O_3, $RhCl_3{\cdot}3H_2O$, and $RhCl(PPh_3)_3$ were used instead of $Rh_4(CO)_{12}$, and the results are shown in Table III. The catalytic activities of Rh_2O_3 and $RhCl_3{\cdot}3H_2O$ were similar to that of $Rh_4(CO)_{12}$, but that of RhCl $(PPh_3)_3$ was very low. These results show that, like Rh4$(CO)_{12}$, $RhCl_3{\cdot}3H_2O$ and Rh_2O_3 are easily converted to an (ethoxycarbonyl)rhodium intermediate. However, $RhCl(PPh_3)_3$ is hard to convert to this intermediate structure. The electron-donating triphenylphosphine ligand suppresses nucleophilic attack of an alkoxide ion on the coordinated carbon monoxide. In the $RhCl_3$–Na_2CO_3 catalytic system, an experiment at a high reaction temperature (180 °C) resulted in no formation of **3b**; the starting material was recovered. The loss of the activity may have been due to the thermal instability of an (ethoxycarbonyl)rhodium intermediate such as $Na[Rh_6(CO)_{15}(COOEt)]$.[8a] Alternate metal carbonyls such as $Co_4(CO)_{12}$, $Ir_4(CO)_{12}$, and $Ru_3(CO)_{12}$ showed no catalytic

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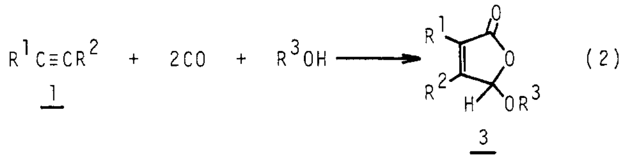
(8) (a) Chini, P.; Martinengo, S.; Giordano, G. *Gazz. Chim. Ital.* **1972**, *102*, 330. (b) Martinengo, S.; Chini, P. *Ibid.* **1972**, *102*, 344.

(9) The ^{1}H NMR spectrum revealed two sets of signals corresponding to a mixture of the meso and racemic isomers, whose spectral data coincided with those in the literature: (a) Gortler, L.; Brandspiegel, K.; Harman, E.; Hecht, S.; Leavitt, R. *J. Org. Chem.* **1973**, *38*, 4048. (b) Rampazzo, L.; Inesi, A. *J. Electrochem. Soc.* **1980**, *127*, 2388.

activity. The starting acetylene was recovered quantitatively in these experiments.

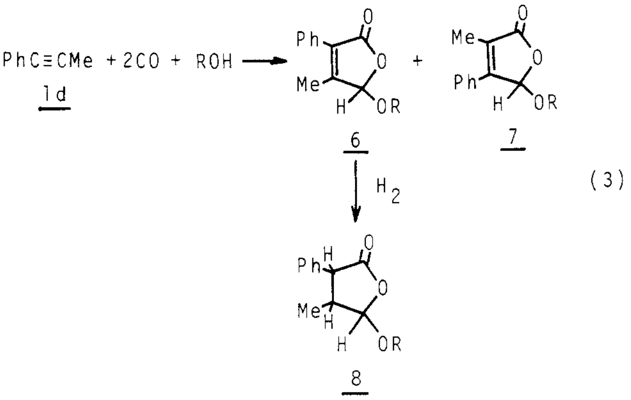
In this reaction system various acetylenes and alcohols could be used to give the corresponding 5-alkoxy-2(5*H*)-furanones **3** (eq 2). These results are summarized in Table IV.



The carbonylations of **1a** in methanol, 1- and 2-propanol, and 1-octanol with the $Rh_4(CO)_{12}$–NaOAc catalyst gave the corresponding 5-alkoxy-3,4-diphenyl-2(5*H*)-furanone, **3a**, **c–e** in 86%, 65%, 60%, and 31% yields, respectively. The reaction in *tert*-butyl alcohol gave no 5-(2-methyl-2-propoxy)-2(5*H*)-furanone. The fact that the yields of **3** decreased with an increase of the size of alcohol suggests the importance of a steric effect in the nucleophilic attack of alkoxide ion on the rhodium carbonyl moiety. A similar trend has been observed in the reaction of $[PtCl(PPh_3)_2(CO)]^+$ with alcohols to form $PtCl(PPh_3)_2(CO_2R)$.[10]

The carbonylation of 2-butyne (**1b**) in ethanol with the $Rh_4(CO)_{12}$-NaOAc catalyst gave 5-ethoxy-3,4-dimethyl-2-(5*H*)-furanone (**3f**) in a 67% yield. Similarly, 5-ethoxy-3,4-diethyl-2(5*H*)-furanone (**3g**) from 3-hexyne (**1c**) was obtained in a 60% yield.

In the reaction of an unsymmetrical acetylene, 1-phenylpropyne (**1d**), 5-alkoxy-4-methyl-3-phenyl-2(5*H*)-furanone (**6**) was the major product accompanied by the other regioisomer, 5-alkoxy-3-methyl-4-phenyl-2(5*H*)-furanone (**7**, eq 3). The isomer ratios of **6** to **7** in methanol and ethanol were 72/28 and 84/16, respectively. The structures of the regioisomers were assigned on the basis of the chemical shift of the methine proton in the 5-position. Thus, the resonances of methine protons in **6a** (R = Me) and **6b** (R = Et) (at δ 5.64 and 5.72) appeared at higher field than those in **7a** (R = Me) and **7b** (R = Et) (at δ 6.08 and 6.12), being consistent with the resonances of methine protons in positions α to the alkyl substituents in **3f** and **3g** (at δ 5.60 and 5.72); for comparison, in **3a–e** those in positions α to the phenyl substituents were at δ 6.1–6.2. The assignments were also supported by the analysis of the ^1H NMR spectrum of **8a** (R = Me) which was obtained by the hydrogenation of **6a** on Pd/C. The 400-MHz ^1H NMR spectrum showed four sets of the signals (8:2:1:1), suggesting the product **8a** to be a mixture of four diastereomers which resulted from the presence of three consecutive chiral centers on the five-membered ring. The spectrum of the major component indicated two doublets at δ 3.88 (*J* = 9.8 Hz) and 5.37 (*J* = 5.4 Hz) and a multiplet at δ 2.85 as resonances corresponding to three methine protons. A similar regioselectivity in the present carbonylation of **1d** has been observed in the cross-hydrocarbonylation with ethylene.[11]



Experimental Section

IR spectra were determined on a Shimazu IR-27G or a JASCO A-202 spectrometer as a KBr disk or neat. ^1H NMR spectra were recorded on a JEOL C-60HL (60 MHz), JNM-PS-100 (100 MHz), or JNM-FX-400 (400 MHz) spectrometer, and ^{13}C NMR spectra were recorded on a JEOL JNM-FX-100 spectrometer with deuteriochloroform as the solvent and tetramethylsilane as the internal standard. GC/MS spectra were measured on a Hitachi RMU-6MG spectrometer operating with a 1.0 m × 3.0 mm glass column packed with 1% OV-1. For column chromatography, silica gel (Wakogel C-200) was used. Quantitative GC analyses using internal standards were performed on a Shimazu GC-4CM gas chromatograph operating with a 2.0 m × 3.0 mm glass column packed with 3% silicone OV-17 on 80–100-mesh Chromosorb W. All peak areas were determined by electronic integration with the use of a Shimazu Chromatopac E1A integrator. All the melting points and boiling points were uncorrected.

Materials. Diphenylacetylene,[12] 2-butyne,[13] 3-hexyne,[13] $Rh_4(CO)_{12}$,[14] and $RhCl(PPh_3)_3$[15] were prepared according to the published procedures. Carbon monoxide was obtained commercially (99.9+%) and used as received. All other chemicals were commercially available reagents of the best purity and were used without further purification.

General Procedure for the Carbonylations of Diphenylacetylenes (1a) in Alcohols. Into a 150-mL centrifuge tube were added diphenylacetylene, **1a** (10 mmol), a rhodium catalyst (0.1 mmol), a basic sodium salt (1–10 mmol), and an alcohol (50 mL), and the tube was placed into a 200-mL stainless-steel autoclave. The autoclave was flushed three times with carbon monoxide (10 kg/cm^2), pressurized to 50 kg/cm^2, and heated with rocking at the desired temperature for 6 h. The reaction mixture was filtered and the solid residue was washed several times with dichloromethane. The products were analyzed by GC of the combined filtrates, and some products were separated by column chromatography on silica gel and characterized by their IR, NMR, and mass spectra and elemental analysis.

Carbonylation of Diphenylacetylene (1a) in Ethanol. $Rh_4(CO)_{12}/Na_2CO_3$ System. A mixture of **1a** (1.78 g, 10 mmol), $Rh_4(CO)_{12}$ (19 mg, 0.025 mmol), Na_2CO_3 (106 mg, 1.0 mmol), and ethanol (50 mL) was heated at 125 °C under 50 kg/cm^2 of carbon monoxide. GC analysis of the resulting red solution indicated the presence of 2.02 g (72% yield) of 5-ethoxy-3,4-diphenyl-2-(5*H*)-furanone (**3b**), 0.31 g (11%) of 3-(ethoxycarbonyl)-2-phenylindanone (**4**), and 0.13 g (4%) of diethyl (2,3-diphenylsuccinate (**5**). The solvent was removed from the reaction mixture in vacuo, and the residue was recrystallized from ethanol/hexane (60 mL, 1:1) to yield 1.19 g (43%) of **3b** as colorless crystals: mp 137–138 °C; mass MS *m/e* 280 (M^+); IR (KBr) 1760 (C=O), 1655 cm^{-1} (C=C). The mother liquor was chromatographed on a silica gel column. Elution with benzene gave 0.11 g of **5** as a mixture of meso and racemic isomers.[9] Further elution with 4:1 benzene/dichloromethane and 3:1 benzene/dichloromethane gave 0.69 g of **3b** and 0.35 g of **4**, respectively.

$RhCl_3/Na_2CO_3$ System. By use of $RhCl_3{\cdot}3H_2O$ (26 mg, 0.10 mmol) and Na_2CO_3 (1.06 g, 10 mmol), **1a** was carbonylated by a procedure as described above. GC analysis of the resulting red solution showed 42% of **3b**, 8% of **4**, and 14% of **5**.

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(10) Byrd, J. E.; Halpern, J. *J. Am. Chem. Soc.* **1971**, *93*, 1634.

(11) The cross-hydrocarbonylation of **1d** and ethylene in ethanol gave 5-ethyl-4-methyl-3-phenyl-2(5*H*)-furanone as a main product, which had been misinterpreted as 5-ethyl-3-methyl-4-phenyl-2(5*H*)-furanone in our previous reports.[1,2]

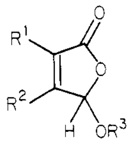
(12) Cope, A. C.; Smith, D. S.; Cotter, R. J. "Organic Syntheses"; 1963; Colect. Vol. IV, p 377.

(13) Brandsma, L. "Preparative Acetylenic Chemistry"; Elsevier: Amsterdam, 1971; pp 29, 146.

(14) Martinengo, S.; Chini, P.; Giordano, G. *J. Organomet. Chem.* **1971**, *27*, 389.

(15) Osborn, J. A.; Wilkinson, G. *Inorg. Synth.* **1967**, *10*, 67.

Table IV.^{a} Synthesis of 5-Alkoxy-2(5*H*)-furanones



furanone				yield,^{b}	
no.	R^1	R^2	R^3	%	^{1}H NMR ($CDCl_3$),^{d} δ
3a	Ph	Ph	Me	86^c	3.62 (s, 3 H, OMe), 6.16 (s, 1 H, CH), 7.2-7.6 (m, 10 H, 2 Ph)
3b	Ph	Ph	Et	87	1.28 (t, 3 H, Me, J = 7.2), 3.6-4.1 (m,2 H, OCH_2), 6.20 (s, 1 H, CH), 7.2-7.6 (m, 10 H, 2 Ph)
3c	Ph	Ph	*n*-Pr	65	0.90 (t, 3 H, Me, J = 7.2), 1.4-1.9 (m, 2 H, CH_2Me), 3.5-4.0 (m, 2 H, OCH_2), 6.18 (s, 1 H, CH), 7.2-7.6 (m, 10 H, 2 Ph)
3d	Ph	Ph	*i*-Pr	60	1.30 (d, 3 H, Me, J = 6.0), 1.32 (d, 3 H, Me, J = 6.0), 4.19 (m, 1 H, OCH), 6.25 (s, 1 H, CH), 7.2-7.6 (m, 10 H, 2 Ph)
3e	Ph	Ph	*n*-C_8H_{17}	31	0.9 (m, 3 H, Me), 1.0-1.4 (m, 12 H, $CH_2(CH_2)_6Me$), 3.6-4.2 (m, 2 H, OCH_2), 6.16 (s, 1 H, CH), 7.2-7.6 (m, 10 H, 2 Ph)
3f	Me	Me	Et	67	1.29 (t, 3 H, CH_2Me, J = 7.2), 1.85 (m, 3 H, Me), 1.98 (m, 3 H, Me), 3.5-4.2 (m, 2 H, OCH_2), 5.60 (br s, 1 H, CH)
3g	Et	Et	Et	60	1.10 (t, 3 H, Me, J = 8.0), 1.16 (t, 3 H, Me, J = 7.5), 1.28 (t, 3 H, Me, J = 7.0), 2.2-2.6 (m, 4 H, CH_2Me), 3.6-4.1 (m, 2 H, OCH_2), 5.72 (br s, 1 H, CH)
6a	Ph	Me	Me	54^c	2.12 (s, 3 H, Me), 3.56 (s, 3 H, OMe), 5.64 (s, 1 H, CH), 7.2-7.6 (m, 5 H, Ph)
7a	Me	Ph	Me	21^c	2.08 (d, 3 H, Me, J = 1.0), 3.48 (s, 3 H, OMe), 6.08 (br s, 1 H, CH), 7.2-7.6 (m, 5 H, Ph)
6b	Ph	Me	Et	78	1.32 (t, 3 H, Me, J = 7.0), 2.16 (s, 3 H, Me), 3.7-4.1 (m, OCH_2), 5.72 (s, 1 H, CH), 7.2-7.6 (m, 5 H, Ph)
7b	Me	Ph	Et	15	1.25 (t, 3 H, Me, J = 7.0), 2.12 (d, 3 H, Me, J = 1.5), 3.7-4.1 (m, OCH_2), 6.12 (br s, 1 H, CH), 7.2-7.6 (m,5 H, Ph)

^{a} Operating conditions: **1a**, 10 mmol; **1b**, 20 mmol; **1c**, 18.5 mmol; **1d**, 20 mmol; R^3OH, 50 mL; CO, 50 kg/cm^2; 125 °C, 6 h; catalyst, $Rh_4(CO)_{12}$ (0.025 mmol)/NaOAc (1.0 mmol). ^{b} Determined by GC. ^{c} At 100 °C. ^{d} J values are given in hertz.

$Rh_4(CO)_{12}$ System. By use of $Rh_4(CO)_{12}$ (19 mg, 0.025 mmol) without a basic sodium salt, the carbonylation of **1a** was carried out, and 11% of **3b**, 27% of **4**, and 3% of **5** were indicated by GC analysis of the resulting orange solution.

Synthesis of 5-Alkoxy-3,4-diphenyl-2(5*H*)-furanones (3). 5-Methoxy-3,4-diphenyl-2(5*H*)-furanone (3a). The Carbonylation of **1a** (10 mmol) in methanol (50 mL) in the presence of $Rh_4(CO)_{12}$ (19 mg, 0.025 mmol) and NaOAc (82 mg, 1.0 mmol) was carried out at 100 °C. The colorless product **3a** (1.90 g) was separated from the reaction mixture by filtration. GC analysis of the filtrate indicated the presence of 0.30 g of **3a**; thus the total yield of **3a** was 86%. Recrystallization of the crude **3a** from benzene/hexane (200 mL, 1:3) afforded pure **3a**: 1.69 g (64%); mp 152-153 °C; MS, *m/e* 266 (M^+); IR (KBr) 1754 (C=O), 1650 cm^{-1} (C=C).

Anal. Calcd for $C_{17}H_{14}O_3$: C, 76.68; H, 5.30. Found: C, 76.55; H, 5.28.

Similarly, the carbonylations of **1a** in several alcohols at 125 °C was carried out by using the $Rh_4(CO)_{12}$/NaOAc system to give the corresponding 5-alkoxy-3,4-diphenyl-2(5*H*)-furanones **3**. Yields and ^{1}H NMR spectra of **3** are summarized in Table IV.

3,4-Diphenyl-5-(1-propoxy)-2(5*H*)-furanone (3c): 65% yield; mp 107-108 °C; MS, *m/e* 294 (M^+); IR (KBr) 1756 (C=O), 1657 cm^{-1} (C=C).

Anal. Calcd for $C_{19}H_{18}O_3$: C, 77.53; H, 6.16. Found: C, 77.55; H, 6.16.

3,4-Diphenyl-5-(2-propoxy)-2(5*H*)-furanone (3d): 60% yield; mp 130-131 °C; MS, *m/e* 294 (M^+); IR (KBr) 1755 (C=O), 1652 cm^{-1} (C=C).

Anal. Calcd for $C_{19}H_{18}O_3$: C, 77.53; H, 6.16. Found: C, 77.50; H, 6.12.

5-(1-Octoxy)-3,4-diphenyl-2(5*H*)-furanone (3e): colorless oil; 31% yield; MS *m/e* 362 (M^+); IR (neat) 1764 cm^{-1} (C=O).

Carbonylation of 2-Butyne (1b) in Ethanol. To a mixture of $Rh_4(CO)_{12}$ (19 mg, 0.025 mmol) and NaOAc (82 mg, 1.0 mmol) in 50 mL of ethanol was added 2-butyne (**1b**; 1.07 g, 20 mmol). The reaction vessel was flushed with carbon monoxide, pressurized to 50 kg/cm^2, and rocked for 6 h at 125 °C. GC analysis of the resulting wine-red solution indicated the presence of 2.08 g (67%) of 5-ethoxy-3,4-dimethyl-2(5*H*)-furanone (**3f**). The reaction mixture was reduced in volume on a rotary evaporator, and the residual brown oil was distilled at reduced pressure to yield 1.69 g of **3f**: colorless oil; bp 74-77 °C (2 mm); 89% pure by GC; MS, *m/e* 156 (M^+); IR (neat) 1766 cm^{-1} (C=O). The analytical sample was purified by preparative GC.

Anal. Calcd for $C_8H_{12}O_3$: C, 61.52; H, 7.74. Found: C, 61.76; H, 7.86.

Carbonylation of 3-Hexyne (1c) in Ethanol. By a procedure similar to that described for 2-butyne, 3-hexyne (**1c**, 1.52 g, 18.5 mmol) was carbonylated. GC analysis of the reaction mixture indicated the presence of 2.05 g (60% yield) of 5-ethoxy-3,4-diethyl-2(5*H*)-furanone (**3g**). The solvent was removed in vacuo, and the residual oil was distilled at reduced pressure to yield 1.73 g of **3g**: colorless oil; bp 85-88 °C (2 mm); 91% pure by GC; MS *m/e* 184 (M^+); IR (neat) 1767 cm^{-1} (C=O). The analytical sample was purified by preparative GC.

Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 65.82; H, 8.93.

Carbonylation of 1-Phenylpropyne (1d) in Alcohols. The carbonylation of **1d** (2.32 g, 20 mmol) in methanol (50 mL) in the presence of $Rh_4(CO)_{12}$ (19 mg, 0.025 mmol) and NaOAc (82 mg, 1.0 mmol) at 100 °C was performed in the same way described for 2-butyne. The solvent was evaporated in vacuo, and the residual oil was crystallized from ethanol (20 mL) to yield 0.89 g of 5-methoxy-4-methyl-3-phenyl-2(5*H*)-furanone (**6a**): colorless crystals; mp 53-54 °C; MS, *m/e* 204 (M^+); IR (KBr) 1765 cm^{-1} (C=O).

Anal. Calcd for $C_{12}H_{12}O_3$: C, 70.57; H, 5.92. Found: C, 70.57; H, 5.89.

The mother liquor was evaporated, and the residual oil was chromatographed on a silica gel column. Elution with hexane/benzene (1:2) gave a mixture of **6a** and the regioisomer, 5-methoxy-3-methyl-4-phenyl-2(5*H*)-furanone (**7a**) (**6a**/**7a** ratio of 3:1) as a colorless oil, which was crystallized from ethanol/hexane (50 mL, 1:4) to give 0.71 g of **6a** as colorless crystals; thus, the total yield of **6a** was 1.60 g (39%). From the mother liquor was obtained 0.83 g of the mixture of **6a** and **7a** (1:1 **6a**/**7a**). The structure of **7a** was assigned on the basis of the ^{1}H NMR spectrum of the mixture. By GC analysis, the presence of 2.21 g (54%) of **6a** and 0.85 g (21%) of **7a** (28:72 **6a**/**7a**) were observed in the reaction mixture.

Similarly, the carbonylation of **1d** in ethanol at 125 °C was carried out by using the $Rh_4(CO)_{12}$/NaOAc system to give 5-ethoxy-4-methyl-3-phenyl-2(5*H*)-furanone (**6b**) and 5-ethoxy-3-

methyl-4-phenyl-2(5*H*)-furanone (**7b**) in 78% and 15% yields, respectively.

6b: colorless oil; MS *m/e* 218; IR (neat) 1765 cm^{-1} (C=O). Anal. Calcd for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47. Found: C, 71.50; H, 6.44.

Hydrogenation of 6a. Into a solution of **6a** (408 mg, 2.0 mmol) in methanol (20 mL) was added Pd/C (5%, 100 mg), and the mixture was stirred for 18 h at room temperature under a hydrogen atmosphere. The catalyst was removed by filtration, and the filtrate was evaporated to give a mixture of diastereomers of 3,4-dihydro-5-methoxy-4-methyl-3-phenyl-2(5*H*)-furanone (**8a**): 406 mg; a colorless oil; IR (neat) 1775 cm^{-1} (C=O). The 400-MHz ^1H NMR spectrum showed four sets of signals: δ 0.69, 0.72, 1.05, and 1.15 for methyl protons and δ 3.52, 3.49, 3.48, and 3.56 for methoxy protons. The isomer ratio (8:2:1:1) was determined from the peak areas of the methoxy protons. The resonances for major component are as follows: δ 0.69 (d, 3 H, Me, *J* = 7.3 Hz), 2.85 (dqd, 1 H, CHMe, *J* = 9.8, 7.3, and 5.4 Hz), 3.52 (s, 3 H, OMe), 3.87 (d, 1 H, CHPh, *J* = 9.8 Hz), 5.37 (d, 1 H, OCHO, *J* = 5.4 Hz), 7.18–7.33 (m, 5 H, Ph).

Carbonylation of 1a in Ethanol in the Presence of $Rh_4(CO)_{12}$ and Various Bases (Table I). Into a 30-mL glass tube containing a Teflon-coated magnetic stirring bar were added **1a** (0.18 g, 1.0 mmol), $Rh_4(CO)_{12}$ (19 mg, 0.025 mmol), a base (1.0 mmol), and ethanol (15 mL), and the tube was placed into a 50-mL stainless-steel autoclave. The autoclave was sealed, flushed twice with carbon monoxide, pressurized to 40 kg/cm^2, and heated with stirring at 125 °C for 6 h. The reaction mixture was analyzed by GC. The results are shown in Table I.

Alcoholysis of 3b. A mixture of compound **3b** (100 mg, 0.36 mmol) and Na_2CO_3 (106 mg, 1.0 mmol) in ethanol (15 mL) was stirred at 150 °C for 6 h under 50 kg/cm^2 of carbon monoxide in the same way described above. GC analysis of the reaction mixture indicated the presence of **5** (81 mg) and **3b** (14 mg).

Registry No. **1a**, 501-65-5; **1b**, 503-17-3; **1c**, 928-49-4; **1d**, 673-32-5; **3a**, 42367-25-9; **3b**, 79379-66-1; **3c**, 79379-68-3; **3d**, 79379-69-4; **3e**, 79379-70-7; **3f**, 79379-71-8; **3g**, 83917-79-7; **4**, 79379-67-2; *meso*-**5**, 13638-89-6; *dl*-**5**, 24097-93-6; **6a**, 83917-80-0; **6b**, 79379-73-0; **7a**, 83917-81-1; **7b**, 79379-72-9; **8a** (isomer 1), 83917-82-2; **8a** (isomer 2), 83946-18-3; **8a** (isomer 3), 83946-19-4; **8a** (isomer 4), 83946-20-7; NaOEt, 141-52-6; NaOH, 1310-73-2; $NaHCO_3$, 144-55-8; Na_2CO_3, 497-19-8; NaOAc, 127-09-3; Li_2CO_3, 554-13-2; K_2CO_3, 584-08-7; Rb_2CO_3, 584-09-8; Cs_2CO_3, 534-17-8; $CaCO_3$, 471-34-1; $BaCO_3$, 513-77-9; LiOAc, 546-89-4; KOAc, 127-08-2; RbOAc, 563-67-7; CsOAc, 3396-11-0; $Rh_4(CO)_{12}$, 19584-30-6; $RhCl_3$, 10049-07-7; Rh_2O_3, 12036-35-0; $RhCl(PPh_3)_3$, 14694-95-2; 5-ethyl-4-methyl-3-phenyl-2(5*H*)-furanone, 79379-62-7; methanol, 67-56-1; ethanol, 64-17-5; 1-propanol, 71-23-8; 2-propanol, 67-63-0; 1-octanol, 111-87-5.

Comparison of the Reactivity of CF_3OX (X = Cl, F) with Some Simple Alkenes

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Reactions of CF_3OX (X = Cl, F) with a variety of simple alkenes were carried out to compare the regio- and stereoselectivity of the additions to carbon–carbon double bonds. The observed addition products with CF_3OCl are consistent with an electrophilic syn addition. With CF_3OF the observed products indicate a different regioselectivity and low stereoselectivity, consistent with a free-radical addition.

Introduction

Fluoroxytrifluoromethane, CF_3OF, was the first carbon compound to contain an OF group bonded to carbon. The compound is easily prepared in high purity by several different methods, and its high thermal stability renders it the most useful derivative for exploring the chemistry of the very reactive O–F bond.[2,3] Trifluoromethyl hypochlorite, CF_3OCl, is a related compound that is also readily obtained.[2,4,5] Its properties are similar to those of CF_3OF as the most suitable perfluoroalkyl hypochlorite for investigative purposes.

Superficially, CF_3OF and CF_3OCl appear to be closely related, and one might expect their reaction chemistry to be very similar. Indeed, both serve as sources of the $CF_3O\cdot$ radical in photochemical reactions.[4b,6,7] However, their reactivity must show substantial differences based on the electronegativity of Cl vs. F.

The chemistry of CF_3OF has been widely investigated, with the greatest interest centered on the ability of CF_3OF to serve as a selective fluorination reagent.[2,8–12] A variety of reactions with both aliphatic and aromatic compounds have been examined. Other fluoroxy reagents have also been examined in less detail and found to undergo analogous reactions.[13,14] In many of the reported reactions of CF_3OF, it has been proposed that the reactions proceed by an electrophilic mechanism involving the concept of

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(1) Work done at Kansas State University, Manhattan, KS 66506.

(2) Mukhametshin, F. *Russian Chem. Rev.* **1980**, *49*, 668.

(3) Lustig, M.; Shreeve, J. M. *Adv. Fluorine Chem.* **1973**, *7*, 175.

(4) (a) Gould, G. E.; Anderson, L. R.; Young, D. E.; Fox, W. B. *J. Am. Chem. Soc.* **1969**, *91*, 1310. (b) Schack, C. J.; Maya, W. *Ibid.* **1969**, *91*, 2902.

(5) Schack, C. J.; Christe, K. O. *Isr. J. Chem.* **1978**, *17*, 20.

(6) Aymonino, P. J. *Photochem. Photobiol.* **1968**, *7*, 761.

(7) Kitazume, T.; Shreeve, J. M. *J. Am. Chem. Soc.* **1977**, *99*, 4194.

(8) Barton, D. H. R. *Pure Appl. Chem.* **1970**, *21*, 285.

(9) Alker, D.; Barton, D. H. R.; Hesse, R. H.; Lister-James, J.; Markwell, R. E.; Pechet, M. M.; Rozen, S.; Takeshita, T.; Toh, H. T. *Nouv. J. Chim.* **1980**, *4*, 239.

(10) Patrick, T. B.; LeFaivre, M. H.; Koertge, T. E. *J. Org. Chem.* **1976**, *41*, 3413.

(11) Hesse, R. H. *Isr. J. Chem.* **1978**, *17*, 60.

(12) Sharts, C. M.; Sheppard, W. A. *Org. React.* **1974**, *21*, 125.

(13) Barton, D. H. R.; Hesse, R. H.; Pechet, M. M.; Tarzia, G.; Toh, H. T.; Westcott, N. D. *J. Chem. Soc. Chem. Commun.* **1972**, 122.

(14) (a) Rozen, S.; Lerman, O. *J. Org. Chem.* **1980**, *45*, 672. (b) Rozen, S.; Lerman, O. *Ibid.* **1980**, *45*, 4122.

0022-3263/83/1948-0242$01.50/0