36 for spectra of isoelectronic d^7 Co^{II} species).

It is less clear from the spectra in Figure 5 how the weak IR band on the side of the e mode is polarized. This uncertainty is completely removed by the difference spectra illustrated in Figure 6. These spectra, obtained by computer subtraction, show that this weak band, arrowed, is polarized in the same direction as the e mode and opposite to the a_1 mode. This supports our original assignment of this band to a matrix splitting of the e mode (qv).

Conclusions

These experiments have finally ended the search for the elusive $Mn(CO)_5$ radical and it is clear that earlier attempts[12] to synthesize $Mn(CO)_5$ in matrices were unsuccessful.[37] $Mn(CO)_5$ has a C_{4v} structure with a probable bond angle of 96 ± 3°. This structure is not wholly unexpected as a d^7 D_{3h} $M(CO)_5$ species would be Jahn-Teller unstable. The IR spectrum of $Mn(CO)_5$ is similar to that of $Re(CO)_5$ and, as expected, the ν_{C-O} bands lie at frequencies between those of the d^6 and d^8 $M(CO)_5$ molecules, $Cr(CO)_5$ and $Fe(CO)_5$, in the matrix.

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(37) G. A. Ozin (private communication, 1981) has pointed out that Mn atoms dimerize very easily, even in highly dilute matrices, and that the species thought to be $Mn(CO)_5$ in ref 12 may well have been an $Mn_2(CO)_x$ fragment.
(38) **Note Added in Proof**: An absorption, 600-900 nm, assigned to $Mn(CO)_5$ has now been observed during the flash photolysis of $Mn_2(CO)_{10}$. Yasufuku, K.; Yesaka, H.; Kobayashi, T.; Yamazaki, H.; Nagakura, S., Proceedings of the 10th International Conference on Organometallic Chemistry, Toronto, 1981.

Palladium-Catalyzed Cyclocarbonylation of Acetylenic Alcohols to Methylene Lactones. Scope and Synthesis of Appropriate Substrates

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Abstract: Methylene lactones are available by catalytic cyclocarbonylation of the ethynyl alcohols resulting from epoxidation and ethynylation of olefins. Dimethylethynylaluminum etherate in toluene is useful for the ethynylation of base-sensitive epoxides. Trans cycloalkanols can be converted to their cis isomers either by oxidation and stereoselective reduction or by epimerization of the corresponding tosylate. The best cyclocarbonylation catalyst system has proved to be $PdCl_2$, anhydrous $SnCl_2$, and 2 equiv of a tertiary phosphine in CH_3CN. A wide variety of methylene lactones, including both cis and trans fused-ring systems, can be made from the appropriate ethynyl alcohol precursors if the substrate concentration is kept sufficiently low to favor cyclization over intermolecular reaction. Incipient ring strain, although it lowers the yield of methylene lactone, does not affect the rate of consumption of starting material, as demonstrated by the competitive cyclocarbonylation of **3c** and **5c**. This observation suggests that the formation of a carboalkoxy intermediate from the catalyst and the substrate alcohol is irreversible.

Interest in synthetic methods for the α-methylene lactone unit has arisen because of the wide spectrum of physiological activity shown by natural products containing it.[2] The unit generally occurs as an α-methylene γ-lactone, most commonly fused to six-, seven-, or ten-membered rings, with both cis and trans stereochemistry observed at the ring junction. A few α-methylene δ-lactones are also found in natural products, fused cis to six-membered rings. A wide variety of other functional groups occur along with the methylene lactone moiety.[2]

Many methods have been developed for the synthesis of the α-methylene lactone unit.[3] Methods involving the introduction of α-methylene group onto a preformed lactone ring[4] have been most widely employed, e.g., in the recent total syntheses of vernolepin,[5a-d] frullanolide,[5e] and eriolanin.[5f,g] These methods necessarily use strongly basic conditions to attack the α position of the lactone—conditions not easily reconciled with the highly functionalized nature of many of the natural-product target molecules. The other approaches which have been suggested[6,7]

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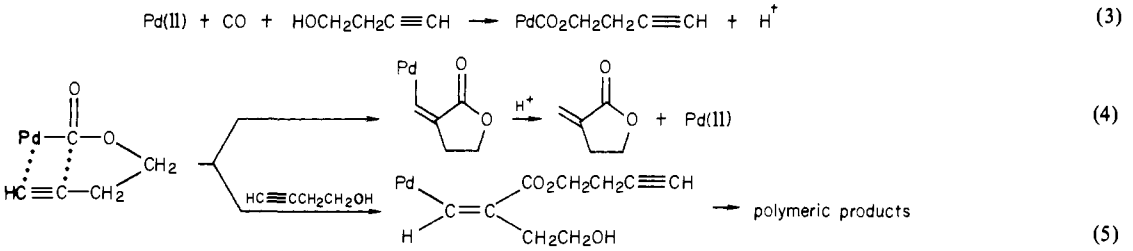
Scheme I

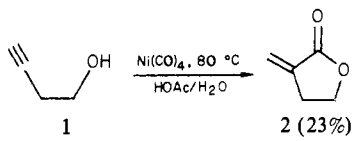


have had limited applicability. For example, the rearrangement of cyclopropylcarbinyl derivatives can give only cis stereochemistry at ring junctions;[6a] the same limitation is also inherent in routes based on the addition of halo ketenes to olefins[7] or other cycloadditions.[6j] The reaction of allyl organometallics (from α-(bromomethyl)acrylic esters) with ketones can give only acyclic and spiro methylene lactones.[6b-e,8]

We therefore attempted to design a generally applicable organometallic synthesis of methylene lactones[9] that could be carried out under mild conditions. An approach that appealed to us was the ring closure of ethynyl alcohols and carbon monoxide, or cyclocarbonylation.[10] Such a reaction would be the final step in a three-step sequence (reaction 1) adding a complete α-methylene γ-lactone unit to a double bond.

$$\text{olefin} \xrightarrow{[O]} \text{epoxide} \xrightarrow{\text{ethynylation}} \text{ethynyl alcohol} \xrightarrow{CO} \text{an } \alpha\text{-methylene } \gamma\text{-lactone} \quad (1)$$

An example of such a cyclocarbonylation had been reported many years ago: the low-yield conversion of 3-butyn-1-ol, **1**, into α-methylene-γ-butyrolactone, **2**, by a stoichiometric $Ni(CO)_4$ reaction (reaction 2).[11] Although this reaction probably involved



1 2 (23%) (2)

a NiH^+ intermediate, attempts to use several transition-metal hydrides as catalysts were discouraging. Furthermore, other reactions catalyzed by metal hydrides—acetylene oligomerization and double-bond migration—were undesirable. We thus examined a catalyst system containing $PdCl_2$ and thiourea, a combination that had been reported to catalyze the carboalkoxylation of acetylene in the presence of air, carbon monoxide, and methanol,[12] as it seemed possible that this system was operating via a nonhydridic pathway. Our initial success[13] in the cyclocarbonylation of 3-butyn-1-ol and *trans*-2-ethynylcyclohexanol prompted further development of the catalyst system, including an investigation of its mechanism of action and of the range of substrates to which it was applicable.

The mechanistic studies, already reported,[14] indicated initial formation (illustrated in Scheme I for 3-butyn-1-ol) of a carboalkoxy species from Pd(II), CO, and the substrate alcohol, followed by intramolecular acetylene insertion (cis addition to the triple bond). Competitive intermolecular insertion of the triple bond in another substrate can occur, leading to dimeric and, eventually, polymeric products. Cleavage of the resulting vinyl–palladium bond by the proton generated in reaction 3 removes the product and regenerates the initial Pd(II) complex. In the course of these studies we were able to design a much more efficient Pd(II) catalyst system with $SnCl_2$ as a cocatalyst.[14] We now report a comparative study of the ability of the various catalyst systems to cyclocarbonylate various substrates, along with some observations on the synthesis of the required ethynyl alcohol precursors.

Results

Comparison of the Catalytic Systems. A modified form of the $PdCl_2$/thiourea carboalkoxylation catalyst is moderately successful for the cyclocarbonylation of ethynyl alcohols to α-methylene γ-lactones (Table I). The intramolecular nature of the present reaction eliminates the complications observed in the carbomethoxylation of acetylene with the original $PdCl_2$/thiourea system, e.g., multiple carboalkoxylation along with dimerization.[12] No such products have been found from the cyclocarbonylation of ethynyl alcohols.

One shortcoming of this catalyst system is the lack of a suitable solvent. In more strongly coordinating solvents, e.g., DMF, the reaction fails completely. Acetone, although usable, does not give a homogeneous reaction mixture; probably for this reason, yields with this system vary considerably from run to run. The catalytic efficiency is low, although the use of sufficient $PdCl_2$ can give reasonable yields, e.g., with *cis*-2-ethynylcyclohexanol (**5a**) (Table I).

The replacement of thiourea by the solubilizing tributylphosphine and the replacement of acetone by acetonitrile give a homogeneous reaction mixture. PdI_2 proves somewhat superior to other palladium halides. More strongly coordinating solvents, e.g., DMF, again suppress the reaction, presumably by inhibiting the coordination of substrate. The use of a second equivalent of added phosphine also suppresses the catalytic reaction completely.

The $PdI_2/Bu_3P/CH_3CN$ system remains homogeneous over at least 5 half-lives in the cyclocarbonylation reaction, which facilitated our study of its mechanism.[14] Dry solvents and substrates prove essential to catalyst life. Rates and yields (Table I) are only slightly better than those obtained with the original $PdCl_2$/thiourea system for the same substrate, e.g., 3-butyn-1-ol.

As Scheme I implies that any Pd(II) complex that can coordinate CO is a potential catalyst, we screened a number of such complexes as catalysts for the cyclocarbonylation reaction. $Pd(CH_3CN)_4^{2+}(BF_4^-)_2$,[15] $[PdL_2Cl]_2^{2+}(BF_4^-)_2$,[16,37] Na_2PdCl_4, and $PdCl_2$ itself all show some activity for the cyclocarbonylation of

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(9) An attempt at using carbene complexes gave discouraging results: Casey, C. P.; Brunsvold, W. R. *J. Organomet. Chem.* **1975**, *102*, 175.

(10) An equally attractive cyclocarbonylation has been reported for 3-bromo-3-buten-1-ols: Matsuda, I. *Chem. Lett.* **1978**, 773.

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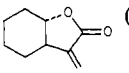
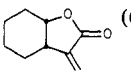
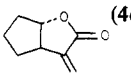
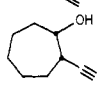
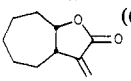
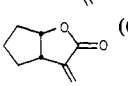
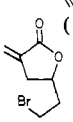
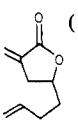
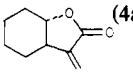
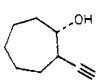
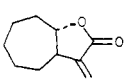
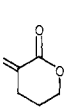
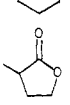
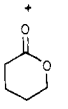
Table I. Catalytic Cyclocarbonylation of Acetylenic Alcohols by Various PdX_2 Systems

acetylenic alcohol, M	PdX_2, M	ligand, M	solvent	T, °C	P_{CO}, atm	time, h	product	% yield	turnovers[a]
 (1), 0.99	$PdCl_2$, 0.05	tu,[b] 0.05	acetone	55	4.8	17	 (2)	21[c]	3.9
 (3a), 2.0	$PdCl_2$, 0.23	tu, 0.23	acetone	50	4.8	17	 (4a)	53[c]	4.1
 (5a), 0.1	$PdCl_2$, 0.1	tu, 0.1	acetone	75	5.1	21	 (6a)	62[d]	
1, 2.74	PdI_2, 0.03	PBu_3, 0.03	CH_3CN	75	7.8	21	2	29[c]	25
1, 1.44	PdI_2, 0.11	PBu_3, 0.11	CH_3CN	75	7.8	21	2	40[c]	3

[a] Moles of alcohol converted to product per mole of Pd. [b] tu = thiourea. [c] GLC yield. [d] Isolated yield.

Table II. Catalytic Cyclocarbonylation of Acetylenic Alcohols by $PdCl_2/SnCl_2/PR_3$ Systems in Acetonitrile

acetylenic alcohol, M	$PdCl_2$, M	$SnCl_2$, M	PR_3, M	T, °C	P_{CO}, atm	time, h	product	% yield[a]	turnovers[b]
 (1), 2.1	0.06	0.06	PBu_3, 0.06	75	7.8	17	 (2)	31	11
1, 1.5	0.07	0.07	PBu_3, 0.14	75	7.8	16	2	70	16
1, 1.0	0.07	0.07	PPh_3, 0.07	75	7.8	17	2	50	8.4
1, 0.99	0.07	0.07	PPh_3, 0.14	75	7.8	10	2	100	17
 (3c), 0.09	0.01	0.01	PPh_3, 0.02	65	5.7	21	 (4c)	27	2.4
 (5b), 0.26	0.09	0.09	PBu_3, 0.18	75	7.8	6	 (6b)	83	2.4
 (5c), 0.09	0.01	0.01	PPh_3, 0.02	65	5.7	1.5	 (6c)	93	8.4
 (10), 0.45	0.055	0.055	PBu_3, 0.11	75	7.8	12	 (18)	77	6.3
 (12), 0.11	0.03	0.03	PPh_3, 0.06	75	7.8	1.5	 (19)	43	1.6
1, 0.57	0.16	0.16	PBu_3, 0.32	75	7.8	13	2	88	3.0
1, 0.30	0.005	0.005	PPh_3, 0.01	75	7.8	1.5	2	97	56
1, 0.30	0.005	0.005	PPh_3, 0.01	75	7.8	4	2	91[c]	
 (3a), 0.24	0.09	0.09	PBu_3, 0.18	75	7.8	6	 (4a)	85	2.2
 (3b), 0.44	0.08	0.08	PBu_3, 0.16	75	7.8	6	 (4b)	71	4.0
 (16), 0.28	0.004	0.004	PPh_3, 0.06	75	5.1	23	 (17)	52	32
 (20), 1.6	0.07	0.07	PPh_3, 0.14	90	7.8	19	 (21)	26	6
							+	14	3
									

[a] GLC yield unless otherwise noted. [b] Moles of alcohol converted to product per mole of Pd. [c] Isolated yield.

3-butyn-1-ol (1), but the yields and catalytic efficiency are both inferior to those shown in Table I for the $PdI_2/Bu_3P/CH_3CN$ system.

The $SnCl_2$ system which we designed in the course of our mechanistic studies[14] gives much better results (Table II) than either of the previous systems. The use of $PdCl_2$ as the palladium halide is crucial; PdI_2 and $SnCl_2$ show very little activity, presumably because of the lower affinity of Sn(II) for I^- than for Cl^-. The use of additional equivalents of $SnCl_2$ has no effect. This system has optimum yield and efficiency at a phosphine:Pd ratio

of 2:1, as shown by the first four runs in Table II. A third equivalent of phosphine stops the reaction entirely, presumably again by blocking the coordination of substrate. Results are somewhat better with triphenylphosphine for acyclic substrates, e.g., 3-butyn-1-ol (**1**), and with tributylphosphine for cyclic substrates which give fused-ring products, e.g., *trans*-2-ethynylcyclohexanol (**3a**). Surprisingly, some catalytic activity remains when no phosphine whatsoever is added.

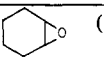
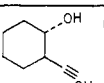
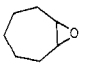
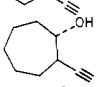
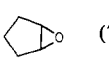
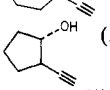
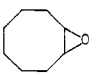
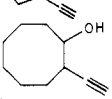
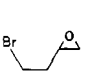
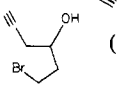
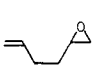
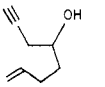
It became apparent during our mechanistic study[14] that intermolecular insertion of the triple bond in another molecule of substrate (reaction 5 in Scheme I), leading to dimeric and polymeric products, can compete for the carboalkoxy intermediate with intramolecular triple bond insertion (reaction 4 in Scheme I) leading to α-methylene lactones. This discovery suggested that yields would improve if the reaction were run at lower substrate concentrations. With use of this strategy, **2** can be obtained from **1** in 91% isolated yield, and high yields and substantial turnover rates can be obtained concurrently. In general dilution increases yield at the expense of rate, because the latter is first order in substrate concentration with the $PdCl_2/SnCl_2/PR_3$ system.[14] Substrate concentrations of 0.3 M appear to strike the proper balance, producing the maximum reaction rate possible without decreasing the ultimate yield for most substrates.

Preparation of Ethynyl Alcohol Substrates. Ethynylation of Epoxides. Successful synthetic use of the cyclocarbonylation reaction requires the availability of appropriate ethynyl alcohol precursors. The three-step sequence from olefins, above, requires the ethynylation of epoxides. Sodium acetylide and LiC≡CH, while they will slowly open epoxides of terminal olefins, are ineffective in ethereal or hydrocarbon solvents at opening epoxides of cyclic olefins.[17] The use of strongly coordinating solvents such as Me_2SO with Li(en)C≡CH[18] enhances the nucleophilicity of the acetylide anion, so that it readily ethynylates cyclic olefins, but also enhances its basicity, making this reagent unsuitable for base-sensitive compounds.

A milder route[19] was suggested by the work of Fried and coworkers in which dialkylalkynylalanes ($R_2AlC{\equiv}CR'$:R = CH_3, Et; R′ ≠ H) are used in nonpolar solvents to open cyclic epoxides, yielding *trans*-2-alkynyl alcohols.[20] The Lewis acid nature of the alanes and their consequent ability to coordinate epoxide oxygens (initial electrophilic attack) facilitate eventual alkynyl transfer. However, the acidic nature of the ethynyl proton renders ethynylaluminum compounds unstable except in the presence of Lewis bases,[21,22] so ethynylation by $R_2AlC{\equiv}CH$ in nonpolar solvents is not feasible. (The use of a protecting group, e.g., Me_3Si, is of course possible, and has been reported by Heathcock and co-workers,[23] but requires an extra step for removal of the protecting group.)

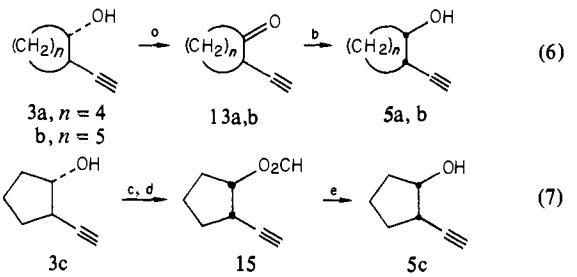
Preliminary experiments with a number of ethynylaluminum species generated from reaction NaC≡CH with the readily available alkylaluminum chlorides[24] suggested the use of dimethylethynylaluminum etherate as an ethynylating agent. (Ether is a Lewis base strong enough to complex and stabilize ethynylaluminums and yet weak enough to be displaced by substrate epoxides.) This can be prepared by the reaction of NaC≡CH with dimethylaluminum chloride in diethyl ether and has been identified by IR and NMR after removal of solvent in vacuo. Addition of epoxide to a toluene solution of the ethynylaluminum etherate with subsequent hydrolysis produces the *trans*-ethynyl alcohol. Results are summarized in Table III.

Table III. Formation of Acetylenic Alcohols by Ethynylation of Epoxides

substrate	product	yield[a] (AlC≡CH reagent)	Li(en)-C≡CH
 (7a)	 (3a)	66[b]	85
 (7b)	 (3b)	30[b]	29
 (7c)	 (3c)	40[b]	84
 (7d)	 (3d)	9	0
 (9)	 (10)	75	15
 (11)	 (12)	64	50

[a] GLC yield unless otherwise noted. [b] Isolated yield.

Scheme II[a]



(6)

(7)

[a] (a) $Na_2Cr_2O_7/H_2SO_4$, Et_2O/H_2O; (b) L-selectride, THF, −78 °C; (c) *p*-TsCl, py; (d) excess $[BzMe_3N][O_2CH]$, CH_3CN, reflux; (e) K_2CO_3, CH_3OH.

Yields are not quantitative for epoxides of cyclic olefins. Some of the initially formed methyl aluminum alkoxide reacts with another equivalent of epoxide to form dimers such as *trans*-2-((*trans*-2-ethynylcyclohexyl)oxy)cyclohexanol (**8**), a reaction which has precedent in the ability of alkylaluminums to catalyze the polymerization of some epoxides.[25] Addition of dilute epoxide to concentrated dimethylethynylaluminum etherate minimizes this side reaction but does not eliminate it. However, the reaction is easy to carry out and the polymeric byproducts are easily removed by distillation or chromatography.

Ethynylation of epoxides by ethynylaluminum reagents is thus a viable alternative to the use of Li(en)C≡CH in Me_2SO (see Table III). The latter procedure gives better yields with substrates which are not base sensitive (e.g., cyclohexene oxide, **7a**), but the ethynylaluminum reagents are more generally applicable. Substrates such as 4-bromo-1,2-epoxybutane (**9**), presumably because of competing elimination reactions, **7d**, and norbornene oxide,[26]

(17) Inhoffen, H. H.; Weissermel, K.; Quinkert, G.; Bartling, D. *Chem. Ber.* **1956**, *89*, 853.

(18) (a) Casadevall, E.; Jallageas, J.-C.; Mion, L.; Mion, M.; Moreau, P. *C. R. Hebd. Seances Acad. Sci.* **1967**, *265*, 839. (b) Carlson, R. G.; Henton, D. E. *J. Chem. Soc. D* **1969**, 674. (c) Carlson, R. G.; Huber, J.-A.; Henton, D. E. *J. Chem. Soc., Chem. Commun.* **1973**, 223.

(19) A preliminary report of this work has been published as a communication: Murray, T. F.; Varma, V.; Norton, J. R. *J. Chem. Soc. Chem. Commun.* **1976**, 907.

(20) (a) Fried, J.; Lin, C. H.; Ford, S. H. *Tetrahedron Lett.* **1969**, 1379. (b) Fried, J.; Sih, J. C.; Lin, C. H.; Dalven, P. *J. Am. Chem. Soc.* **1972**, *94*, 4343. (c) Fried, J.; Sih, J. C. *Tetrahedron Lett.* **1973**, 3899.

(21) (a) Parrini, P.; Pansini, P. French Patent, 1 343 923; *Chem. Abstr.* **1964**, *61*, 1892g. (b) Wilke, G.; Schneider, W. *Bull. Chim. Fr.* **1963**, 1462. (c) Demarne, H.; Cadiot, P. *Ibid.* **1968**, 205. (d) Lehmkuhl, H.; Zeigler, K. In "Methoden der Organischen Chemie"; Part 4; Georg Thieme Verlag: Stuttgart, 1970; Vol. XIII, pp 157–158 and references therein.

(22) Demarne, H.; Cadiot, P. *Bull. Soc. Chim. Fr.* **1968**, 216.

(23) Chavdarian, C. G.; Woo, S. L.; Clark, R. D.; Heathcock, C. H. *Tetrahedron Lett.* **1976**, 1769. The product ethynyl alcohol is cyclocarbonylated to an α-methylene lactone by the original $PdCl_2$/thiourea system. The ethynyl alcohol contains a vinyl substituent stereochemically well situated for competitive cyclocarbonylation to a saturated lactone, which may account for the mediocre yield of methylene lactone.

(24) For details on all aluminum species studied see Ph.D. thesis of T. F. Murray, Princeton University, 1978.

(25) Hoffman, E. G. *Justus Liebigs Ann. Chem.* **1960**, *629*, 104.

presumably because of base-catalyzed transannular reactions, give very poor yields of ethynyl alcohols with Li(en)C≡CH and much better ones with the ethynylaluminum reagents. Both reagents transfer ethynyl groups to the unsubstituted carbon of epoxides of terminal olefins. Being Lewis acids, the ethynylaluminum reagents do produce rearranged ethynyl alcohols from susceptible substrates, e.g., 2-*exo*-7-*syn*-norbornanol from *exo*-norbornene oxide.[26]

***cis*-2-Ethynylcycloalkanols.** *cis*-2-ethynylcycloalkanols can easily be prepared by epimerization of the corresponding trans compounds (Scheme II). Oxidation of *trans*-2-ethynylcyclohexanol and -cycloheptanol, **3a** and **3b**, best accomplished with a two-phase chromic acid system,[18b,27] produces the unstable ketones **13** (not isolated).

A small amount of isomerization of the ethynyl group to the corresponding allene is observed; similar complications in oxidation of ethynyl alcohols have been reported elsewhere.[28] Immediate reduction of the ketones **13** with L-selectride[29] gives the desired *cis*-2-ethynylcycloalkanols **5** with at least 95% stereoselectivity (reaction 6).[30] The yield of *cis*-2-ethynylcyclohexanol, **5a**, from the *trans*-**3a** is 51%; that of *cis*-2-ethynylcycloheptanol, **5b**, from **3b** is 66%.

With *trans*-2-ethynylcyclopentanol, **3c**, we found clean oxidation impossible. However, *cis*-2-ethynylcyclopentanol, **5c**, previously reported as a product of the reductive cleavage of an acetylenic epoxide,[28] proved available by conversion of **3c** to its tosylate, **14**, epimerization of **14** by displacement of tosylate by formate ion, and methanolysis of the resulting formate **15**. With 7 equiv of benzyltrimethylammonium formate epimerization proceeded with 97% inversion of configuration of carbon (reaction 7).

Scope of the $PdCl_2/SnCl_2/PR_3$ Catalytic Cyclocarbonylation System. As shown in Table II, catalytic cyclocarbonylation can produce a wide variety of methylene lactones. Both *trans*- and *cis*-ethynyl alcohols readily give fused-ring methylene lactones of corresponding stereochemistry.[30] For six- and seven-membered rings (see also Table I) yields are about the same for cis and trans ring fused lactones; the results with five-membered rings (where the *trans*-ethynyl alcohol leads to a somewhat strained product) will be discussed below. In the formation of fused-ring products we have not found it possible to achieve the simultaneous high yields and turnover rates obtained with **1** as substrate; nevertheless, good yields are possible if sufficient $PdCl_2$ is used.

The $PdCl_2/SnCl_2/PR_3$ catalyst system is even capable of producing α-methylene δ-lactones. Unlike previous catalyst systems, which were capable of producing an α-methylene δ-lactone only if the ethynyl and hydroxyl groups were fixed on an appropriate rigid skeleton,[26] the $PdCl_2/PR_3$ system catalyzes the cyclocarbonylation of 4-pentyn-1-ol, **16**, to α-methylene-δ-valerolactone, **17** (Table II).

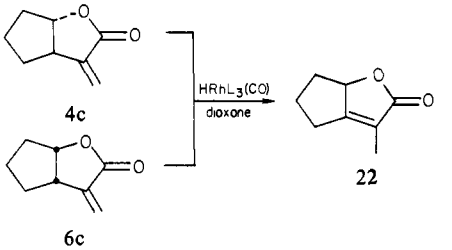
The catalyst system is also successful with acyclic ethynyl alcohols containing other functional groups. It cyclocarbonylates **10**, which has a bromo substituent, in good yield; it cyclocarbonylates **12**, which has a vinyl substituent attached by a side chain, in somewhat reduced yield (Table II).[31] The successful use of acetone and acetonitrile as solvents suggests tolerance of ketones and nitriles.

The low yield in the cyclocarbonylation of the vinyl-substituted **12**, however, prompted us to investigate whether a carbon–carbon double bond could become involved in cyclocarbonylation. It has proven possible to cyclocarbonylate 3-buten-1-ol (**20**), although in order to proceed at a significant rate the reaction requires a higher temperature than the cyclocarbonylation of acetylenic alcohols (Table II). The fact that significant valerolactone is formed along with α-methylbutyrolactone suggests that the olefinic analog of reaction 4 in Scheme I may be less regioselective than is reaction 4 itself. Vinyl groups thus have some reactivity in cyclocarbonylation, a fact which may explain the mediocre yields obtained by Heathcock and co-workers[23] using the original $PdCl_2$/thiourea system on a fused-ring substrate with a vinyl substituent. As no byproducts were reported despite complete disappearance of starting material, intermolecular complications (which could have been avoided by the use of lower concentrations) may also have been a factor.

Unsaturated alcohols with only one saturated carbon cannot be cyclocarbonylated. Rather than the formation of highly strained α-methylene or α-methyl β-lactones, propargyl alcohol and allyl alcohol undergo intermolecular carboalkoxylation to give polymeric material. Cyclocarbonylation of acetylenic alcohols where the triple bond is internal is also unsuccessful. *trans*-2-Propynylcyclohexanol gives no significant yield of α-ethylidene-γ-butyrolactone—a consequence of the comparative unreactivity of internal triple bonds in reactions like reaction 4 (Scheme I).[14] Finally, cyclocarbonylation is not feasible for ethynylphenols. An attempt with *o*-ethynylphenol[32] rapidly deposited Pd metal and left most of the starting material unreacted after 18 h at 70 °C.

A Strained Fused Ring Methylene Lactone. Influence of Product Strain on the Rate of Catalytic Cyclocarbonylation. As noted above and shown in Table II, when we attempted the catalytic cyclocarbonylation of *trans*-2-ethynylcyclopentanol (**3c**), we obtained in reduced yield (27%) a product tentatively identified as the fused-ring product **4c** (Table II). One would expect **4c** to be significantly strained; the corresponding fully saturated hydrocarbon, *trans*-bicyclo[3.3.0]octane, is 6 kcal/mol more strained than the corresponding cis compound.[33] The strain of such a system is also reflected in the fact that the corresponding unsubstituted lactone does not readily form from *trans*-2-hydroxycyclopentaneacetic acid.[34]

Confirmation of the trans-fused methylene lactone structure has been obtained by the following method. Ali and Roberts[7a] and Hassner and co-workers,[7b] using a sequence beginning with a [2 + 2] cycloaddition, have unequivocally synthesized the cis isomer **6c**—the same compound which we obtained by the cyclocarbonylation of **5c**. Upon treatment with the isomerization catalyst $HRh(PPh_3)_3(CO)$ in dioxane,[35] both isomeric methylene lactones isomerize to the same butenolide (**22**), thus proving that the product of our cyclocarbonylation reaction is indeed the strained trans-fused α-methylene lactone (reaction 8).

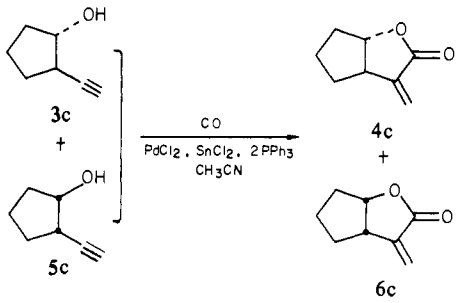


(8)

The Influence of Product Strain on Cyclocarbonylation Rates. Thus the cis **5c** can be cyclocarbonylated to the comparatively

(26) Murray, T. F.; Varma, V.; Norton, J. R. *J. Org. Chem.* **1978**, *43*, 353.
(27) Brown, H. C.; Garg, C. P. *J. Am. Chem. Soc.* **1961**, *83*, 2952.
(28) Carlson, R. G.; Cox, W. W. *J. Org. Chem.* **1977**, *42*, 2382.
(29) Brown, H. C.; Krishnamurthy, S. *J. Am. Chem. Soc.* **1972**, *94*, 7159.
(30) We have not succeeded in preparing the *cis*-ethynyl cycloalkanols free of traces of the trans isomers. In the case of **5a** and **5b**, it is not clear whether these traces arise from incomplete oxidation of starting materials or from lack of complete stereospecificity in the ketone reduction. In the case of **5c**, the fact that the epimerization reaction 7 is not completely stereospecific leads to a product (**5c**) containing 3% of the trans isomer **3c**. The cis ring fused lactones obtained upon cyclocarbonylation thus contain traces of their trans isomers.
(31) Some isomerization of **19** (apparently of the side chain double bond) occurs after prolonged reaction but does not begin until the starting material **12** has been completely consumed. In general, the methylene lactone products are stable under the reaction conditions.
(32) Prey, V.; Pieh, G. *Monatsh.* **1949**, *80*, 790; Odaira, Y. *Bull. Chem. Soc. Jpn.* **1957**, *29*, 470. Previously unreported spectral data for *o*-ethynylphenol are as follows: NMR ($CDCl_3$) δ 7.6–8.5 (m, 4 H), 6.1 (s, 1 H, OH), 3.38 (s, 1 H, ≡CH); IR (neat) 3500, 3282, 2098, 1482, 1222, 752 cm^{-1}.
(33) Chang, S.; McNally, D.; Shary-Tehrany, S.; Hickey, M. J.; Boyd, R. H. *J. Am. Chem. Soc.* **1970**, *92*, 3109.
(34) Meyers, A. I.; Mihelich, E. D.; Nolen, R. L. *J. Org. Chem.* **1974**, *39*, 2783.
(35) Strohmeier, W. *J. Organomet. Chem.* **1973**, *60*, C60.

unstrained **6c** in good yield, while the trans **3c** can be cyclo-



(9)

carbonylated to the strained **4c** in considerably lower yield under the same conditions. These facts suggested that a comparison of the relative cyclocarbonylation rates would prove instructive. We therefore cyclocarbonylated a mixture of **3c** and **5c** at 65 °C and 5.7 atm of CO and monitored the rates of disappearance of **3c** and **5c** and the rates of appearance of the strained product **4c** and the unstrained product **6c**. The substrates **3c** and **5c** were consumed at the same rate, although the unstrained cis product

$$d[5c]/dt = -k_{obsd}(cis)[5c]$$

$$d[3c]/dt = -k_{obsd}(trans)[3c]$$

$$k_{obsd}(cis)/k_{obsd}(trans) = 1.01 \pm 0.10$$

6c was formed in twice the yield of the strained product **4c**. In other words, product ring strain manifests itself in a smaller fraction of cyclic product formation rather than in a slower net rate of reaction.

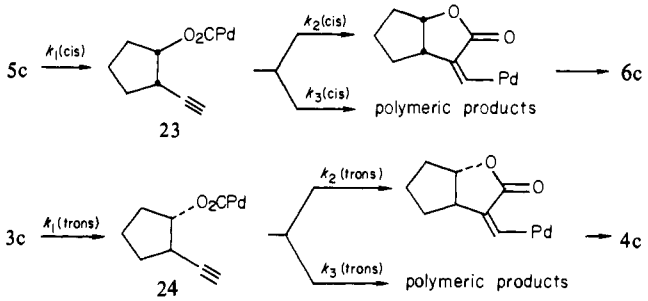
Discussion and Conclusions

The best catalytic system for cyclocarbonylation is $PdCl_2$ with 1 equiv of anhydrous $SnCl_2$ and 2 equiv of a tertiary phosphine in dry acetonitrile. 3-Butyn-1-ol (**1**) can be converted to **2** in near-quantitative yield with high catalytic efficiency, but the synthesis of fused-ring methylene lactones in good yields requires the use of comparatively large amounts of catalyst. As both *cis*- and *trans*-2-ethynylcycloalkanols are readily available, catalytic cyclocarbonylation is capable of producing both cis and trans ring fused methylene lactones readily from olefinic precursors. The use of concentrations sufficiently low to favor cyclization over intermolecular reaction is crucial. The presence of a carbon–carbon double bond in an acetylenic alcohol may permit competing reactions and give reduced yields of methylene lactone.

Comparison of the cyclocarbonylation of **3c**, *trans*-2-ethynylcyclopentanol (which gives the strained trans fused methylene lactone **4c** as product), with that of **5c**, *cis*-2-ethynylcyclopentanol (which gives the comparatively unstrained cis methylene lactone **6c**), shows the effect of product ring strain on cyclocarbonylation. Incipient ring strain does not affect the rate of consumption of starting material but changes the yield of methylene lactone from starting material, implying a decrease in the fraction of some intermediate which goes on to methylene lactone product.

A plausible explanation of these results is that the intermediate involved is the carboalkoxy species in Scheme I (eq 3 and 4). The resulting interpretation is illustrated in Scheme III, where k_1 is the rate of carboalkoxy formation, k_2 is the rate of intramolecular insertion, and k_3 is the rate of intermolecular insertion of another substrate triple bond into the carboalkoxy Pd–C bond. If we assume that k_1^{cis} is approximately equal to k_1^{trans} *and that carboalkoxy formation is irreversible* under catalytic conditions as shown in Scheme III, **5c** and **3c** will be consumed at the same rate, as observed; as strain should make k_2^{trans} considerably slower than k_2^{cis}, making k_2^{cis}/k_3^{cis} larger than k_2^{trans}/k_3^{trans} (one would expect k_3^{cis} to be approximately equal to k_3^{trans}), the unstrained cis product **6c** will be formed in higher yield than the strained trans product **4c**—also as observed. If carboalkoxy formation were reversible, the slower rate ($k_2^{trans} + k_3^{trans}$) at which products are formed from **24** would be reflected in a slower net rate of consumption of **3c**—in disagreement with the observation that k_{obsd}^{trans} is approximately equal to k_{obsd}^{cis}.[36] This interpretation, with its implication that carboalkoxy formation (reaction 3 in Scheme I) is *irreversible* under the conditions of these reactions, is quite consistent with our earlier finding[14] that formation of such carboalkoxy intermediates is rate determining.

Scheme III



Experimental Section

Toluene, THF, and ether were distilled under N_2 from sodium benzophenone ketyl. Acetone was distilled from K_2CO_3 under nitrogen. Dimethyl sulfoxide was dried over 3A molecular sieves. 1,4-Dioxane was purified by passage through a column of Grade-I neutral Al_2O_3, stored in a refrigerator in a brown bottle over 3A molecular sieves, and purged with N_2 prior to use. Acetonitrile was distilled under N_2 from P_2O_5 onto CaH_2, and redistilled under N_2 prior to use.

Analytical GLC was done with the following $^1/_4$-in. aluminum columns: (A) 8-ft 5% DEGS on 60–80 mesh Chromosorb PNAW, (B) 9-ft 10% OV-101 on 60–80 Chromosorb W-HP, (C) 12-ft 3% DEGS (H_3PO_4 stabilized) on 70–80 Chromosorb G-AW, (D) 12-ft 3% OV-17 on 70–80 Chromosorb G-AW-DMCS. Preparative GLC was done with a $^3/_8$-in. aluminum column of 5% DEGS on 60–80 mesh Chromosorb PNAW.

General Procedure for Cyclocarbonylation of Ethynyl Alcohols. The catalysts were prepared by placing the ingredients—Pd salt, ligand, and cocatalyst—in the following apparatus. A brass cross-tee fitted with a stainless-steel adapter was connected to a 6-oz Fischer-Porter pressure vessel, sealed by a Viton A O-ring. The cross-tee was also fitted with a ball valve in the arm directly above the pressure vessel (allowing addition of liquids and withdrawal of aliquots by syringe), with a needle valve connected to a carbon monoxide source, and with a brass tee fitted with a pressure gauge and pressure release safety valve. Sequential use of the needle valve and the ball valve allowed flushing of the apparatus with carbon monoxide.

Dry solvent was then introduced by syringe into the pressure vessel through the ball valve; the system was flushed twice with CO and lowered into an oil bath at the desired temperature. The CO pressure was increased to the desired level, and the mixture was magnetically stirred for 1 h or until homogeneous.

Substrate was then introduced by syringe through the ball valve. The reaction vessel was flushed with CO and then pressurized to the desired level. When no more substrate remained (by GLC analysis) or the catalyst had become inactive (no change observed between consecutive GLC analyses), the vessel was allowed to cool and the CO pressure released.

Cyclocarbonylation of 3-Butyn-1-ol (1) to α-Methylene-γ-butyrolactone (2). $PdCl_2$/tu System. To a stirring suspension of $PdCl_2$ (0.051 g, 0.29 mmol) and thiourea (tu) (0.022 g, 0.29 mmol) in 5 mL of acetone was added 3-butyn-1-ol, **1** (0.371 g, 5.3 mmol). The vessel was flushed with CO, then pressurized to 50 psi, and stirred 17 h at 70 °C. Removal of solvent from the reaction solution was followed by vacuum distillation, addition of hexamethylenediol as a standard, and GLC analysis (column A) showing a 21% yield of α-methylene-γ-butyrolactone **2**. Spectroscopic data agreed with those reported.[6k]

(36) If one added to Scheme III back-reaction rates $k_{-1}(cis)$ and $k_{-1}(trans)$ for the return of **23** and **24** to **5c** and **3c**, the steady-state approximation in **23** and **24** would give an expression for the rate of disappearance of the substrates:

$$\frac{d[S]}{dt} = -k_{obsd}[S] = -\left(k_1 - \frac{k_1 k_{-1}}{k_{-1} + k_2 + k_3}\right)[S] = -\frac{k_1(k_2 + k_3)}{k_{-1} + k_2 + k_3}[S]$$

If $k_2^{(cis)} > k_2^{(trans)}$ and the other rate constants were about the same in the two systems, $k_{obsd}(cis)$ would be greater than $k_{obsd}(trans)$ and the cis-**5c** would be consumed faster than the *trans*-**3c**.

(37) Dixon, K. R.; Hawke, D. J. *Can. J. Chem.* **1971**, *49*, 3252.

$PdCl_2/SnCl_2/PPh_3$ System. To a solution of naphthalene (0.063 g, 0.49 mmol), $PdCl_2$ (0.014 g, 0.08 mmol), PPh_3 (0.042 g, 0.16 mmol), and anhydrous $SnCl_2$ (0.015 g, 0.08 mmol) in 15 mL of CH_3CN at 75 °C was added **1** (0.333 g, 4.75 mmol), and the solution was stirred 90 min under 7.8 atm of CO. Aliquots were taken by syringe every 10 min throughout the reaction period. The vessel was flushed with CO after every sampling and then repressurized. GLC analysis (column A, 160 °C) of the 90-min aliquot indicated no remaining **1** and a 97% yield of **2**.

In a similar reaction **1** (0.70 g, 10 mmol) was added to a solution of $PdCl_2$ (0.028 g, 0.16 mmol), anhydrous $SnCl_2$ (0.030 g, 0.16 mmol), and PPh_3 (0.084 g, 0.32 mmol) in 30 mL of CH_3CN at 75 °C, and the mixture was then stirred under 100 psi of CO for 4 h. The resulting solution was reduced in volume on a rotary evaporator, taken up in 300 mL of diethyl ether, and then passed through a 4 in. × 1 in. silica gel column to remove Pd complexes and metal. The Et_2O was removed in vacuo, and the resulting yellow oil was distilled at reduced pressure to yield **2** (0.89 g, 9.1 mmol, 91%): bp 89–90 °C (13 mmHg), 99% pure by GLC (column A).

Cyclocarbonylation of *trans*-2-Ethynylcyclohexanol (3a) to 4a by $PdCl_2/SnCl_2/PBu_3$ System. To a solution of $PdCl_2$ (0.081 g, 0.46 mmol), anhydrous $SnCl_2$ (0.087 g, 0.46 mmol), PBu_3 (0.186 g, 0.92 mmol) in 5 mL of CH_3CN at 75 °C was added **3a** (0.149 g, 1.2 mmol), and the reaction was stirred 6 h under 7.8 atm of CO. GLC analysis (column A) of the reaction mixture indicated an 85% yield of **4a** (1.02 mmol). Spectroscopic data on a sample isolated by preparative GLC agreed with those reported in the literature.[6f] Anal. ($C_9H_{12}O_2$): C, H.

In a similar manner, **3b** and **5b** were cyclocarbonylated to the known[6f] α-methylene lactones **4b** and **6b**, respectively (Table II).

Preparation of 4-Bromo-1,2-epoxybutane (9) and 4,6-Epoxy-1-hexene (11). The epoxides **9** and **11** were prepared from 4-bromo-1-butene and 1,5-hexadiene, respectively, with *m*-chloroperbenzoic acid according to a standard procedure.[38] For **9**: bp 69–70 °C (30mmHg); ^1H NMR ($CDCl_3$) δ 1.85–2.35 (m, 2 H), 2.7–3.2 (m, 3 H), 3.50 (t, 2 H). For **11**: bp 133 °C (760mmHg); ^1H NMR ($CDCl_3$) δ 1.4–1.9 (m, 4 H), 2.05–3.2 (m, 3 H), 4.8–5.25 (m, 2 H), 5.5–6.2 (m, 1 H).

Dimethylethynylaluminum Etherate. A 30-mL sample of a 2.0 M toluene solution of dimethylaluminum chloride (60 mmol) was added by syringe over 1 min to a suspension of 3.2 g (66 mmol) of NaC≡CH stirring in 60 mL of Et_2O at 0 °C under a nitrogen atmosphere. The resulting mixture was stirred at room temperature for 5 h. Precipitated NaCl was filtered off under N_2 using standard Schlenk apparatus.[39] The resulting yellow filtrate was then reduced in volume by removal of solvent in vacuo to 15–20 mL (3–4 M) for use in ethynylation of epoxides.

Removal of all soivent from a solution prepared in this manner yielded a yellow oil identified spectroscopically[40] as dimethylethynylaluminum diethyl etherate: ^1H NMR (C_6D_6) δ −0.62 (br s, 6 H, CH_3Al), 1.05 (t, J = 7 Hz, 6 H), 2.05 (s, 1 H, ≡CH), 3.82 (q, J = 7 Hz, 4 H); IR (Nujol) 3250, 1960 cm^{-1}.

General Procedure for Reaction of Epoxides with Dimethylethynylaluminum Etherate. *trans*-2-Ethynylcyclohexanol (3a) from Me_2AlC≡CH·Et_2O. To a concentrated solution of 118 mmol of Me_2AlC≡CH·Et_2O (from 30 mL of 2 M dimethylaluminum chloride and 6.4 g of NaC≡CH) was added a 10% solution in toluene of cyclohexene oxide **7a** (5.15 g, 52.5 mmol) over 45 min with vigorous stirring at room temperature. The mixture was stirred for 15 min after completion of addition, then chilled to 0 °C, and hydrolyzed carefully by dropwise addition of H_2O. The resulting gel was diluted with 100 mL of anhydrous Et_2O before addition of $MgSO_4$. The dried solution was filtered and the cake washed with 10 × 30 mL of Et_2O. Removal of solvent on a rotary evaporator resulted in a viscous yellow liquid which upon distillation (bp 103–105 °C (35mmHg)) gave the known[28] **3a** (3.82 g, 31 mmol, 58%) which was identified by comparison of its spectra (IR, NMR) with reported values.

In a directly analogous manner cycloheptene oxide (**7b**), cyclopentene oxide (**7c**), and cyclooctene oxide (**7d**) were converted to the corresponding known[28] *trans*-ethynylcycloalkanols **3b**, **3c**, and **3d** in 30, 40, and 9% yield, respectively. The alcohols were identified by comparison of their IR and NMR spectra with reported values.[28]

Isolation of *trans*-2-((*trans*-2-Ethynylcyclohexyl)oxy)cyclohexanol (8) from Ethynylation of Cyclohexene Oxide with Aluminum Reagent. Cyclohexene oxide (1.92 mL, 19 mmol) was treated with a toluene solution of diethylethynylaluminum etherate (32 mmol), prepared from diethylaluminum chloride (17.5 mL of 1.8 M solution in toluene) and 1.8 g of NaC≡CH in a manner analogous to that described above. Hydrolysis and workup by the same procedure gave a yellow oil which was vacuum distilled. The fraction (0.7 g) boiling above 119 °C (0.2mmHg) deposited **8** as a white solid on standing at −20 °C. The supernatant liquid was decanted, and the solid was washed with several portions of pentane and dried in vacuo: mp 92–94 °C; NMR ($CDCl_3$) δ 3.55 (s, 1 H), 3.4 (m, 3 H), 2.5 (approximately dd, 1 H, J = 2, 12 Hz), 2.20 (d, 1 H, J = 2 Hz), 2.15–1.65 (m, 8 H), 1.6–1.0 (m, 8 H); IR (KBr) 3518, 3220, 1095 cm^{-1}. Anal. ($C_{14}H_{22}O_2$): C, H.

1-Bromo-hex-5-yn-3-ol (10). In the same manner as the above ethynylation of cyclohexene oxide, 4-bromo-1,2-epoxybutane **9** (4.07 g, 27 mmol) was treated with dimethylethynylaluminum etherate, yielding a yellow viscous oil that upon purification by medium-pressure liquid chromatography (silica gel, 20% ethyl acetate/hexane) gave **10** (3.60 g, 20.3 mmol, 75%): bp 36–42 °C (0.2 mm); NMR ($CDCl_3$) δ 1.9–2.8 (m, 6 H), 3.62 (t, 2 H, CH_2Br), 4.05 (m, 1 H, $CHOH$); IR (CH_2Cl_2) 3500 (br), 3300, 2120 cm^{-1}. Anal. (C_6H_9OBr): C, H, Br.

Oct-7-en-1-yn-4-ol (12) was prepared in a like manner from **11** and Me_2AlC≡CH·Et_2O in 64% yield: bp 55 °C (5 mm); NMR ($CDCl_3$) δ 1.25–2.6 (m, 8 H), 5.2 (m, 2 H), 5.5–6.2 (m, 1 H); IR (neat) 3500, 3300, 2120, 1640 cm^{-1}. Anal. ($C_8H_{12}O$): C, H.

Synthesis of Ethynyl Alcohols by Treatment of Epoxides with Li(en)C≡CH. A typical procedure for obtaining the ethynyl alcohols via Li(en)C≡CH is that used for **3b**. To a suspension of Li(en)C≡CH (66 g, 717 mmol) in 150 mL of Me_2SO under N_2 was added cycloheptene oxide (28 mL, 27.2 g, 242 mmol) and the mixture stirred at room temperature for 48 h. It was then hydrolyzed with a saturated NH_4Cl solution and extracted with 20 × 25 mL of Et_2O. The ether fractions were dried over $MgSO_4$, and the ether was removed. The resulting yellow oil was distilled at reduced pressure (115 °C (27mmHg)) to yield the known[28] **3b** (9.7 g, 70.2 mmol, 29%).

***trans*-2-Ethynylcyclopentanol (3c).** A 20-g (0.233-mol) sample of cyclopentene oxide (**7c**) and 64.2 g (0.730 mol) of lithium ethylenediamine acetylide in 150 mL of Me_2SO were reacted 36 h at room temperature. Hydrolysis and extraction as described above for **3b**, followed by vacuum distillation (bp 77–83 °C (14 mm)) gave 21.6 g (0.196 mol, 85%) of **3c**, of 99% purity by GLC (column B). The NMR spectrum of **3c** was identical with that reported.[28]

2-Ethynylcyclohexanone (13a). A solution of **3a** (4.97 g, 40 mmol) in Et_2O (20 mL) was placed in a flask fitted with a mechanical stirrer and dropping funnel. To this was added at 0 °C—dropwise with stirring—a chromic acid solution prepared from 12 g of $Na_2Cr_2O_7 \cdot 2H_2O$, first dissolved in 9 mL of concentrated H_2SO_4 and then diluted with H_2O to 60 mL. This mixture was stirred 2 h at 0 °C after which time IR examination of an aliquot showed that some alcohol remained unoxidized. A 30 mol % sample of more chromic acid (prepared as above) was added and the solution stirred an additional hour. The solution was then extracted with ether, washed with a saturated $NaHCO_3$ solution, dried over $MgSO_4$, filtered, and evaporated in vacuo to yield the known[28] 2-ethynylcyclohexanone (**13a** (3.0 g, 24.5 mmol), 61% of crude material).

***cis*-2-Ethynylcyclohexanol (5a).** To a solution of **13a** (2.44 g, 20 mmol) in 20 mL of THF at −78 °C was added 22 mL of 1 M L-selectride, and the mixture was stirred 3 h at −78 °C. The solution was then hydrolyzed with 1 mL of H_2O. A mixture of 7.3 mL of 2 N NaOH (22 mmol) and 8.8 mL of 10% H_2O_2 (72 mmol) was added for oxidative removal of the boron, and the reaction was stirred 1 h at 45 °C. The aqueous layer was then saturated with K_2CO_3; an emulsion formed between the organic and aqueous layers. The organic layer was decanted and the emulsion extracted with 3 × 20 mL of Et_2O. The combined organic fractions were then dried over $MgSO_4$, and the solvent was removed in vacuo to yield a red oil that upon distillation gave the known[28] *cis*-2-ethynylcyclohexanol **5a** (1.5 g, 13.8 mmol, 69%), which was spectroscopically characterized by comparison with reported values; bp 45 °C (0.2 mm). Its 3,5-dinitrobenzoate derivative had a melting point of 104–105 °C. Anal. ($C_{15}H_{14}N_2O_6$): C, H, N.

The overall yield of **5a** in two steps from **3a** can be as high as 51% if the unstable ethynyl ketone is reduced immediately after its preparation.

2-Ethynylcycloheptanone (13b)[18b,28] was similarly prepared from **3b** and reduced to the known[28] *cis*-2-ethynylcycloheptanol (**5b**) in 66% overall yield.

***trans*-2-Ethynylcyclopentyl Tosylate (14).** *p*-Toluenesulfonyl chloride (17.3 g, 91 mmol) and 5.0 g (45 mmol) of **3c** were dissolved in 70 mL of pyridine and refrigerated for 40 h. Isolation and purification by standard procedures[41] gave 9.64 g (36.5 mmol, 80%) of white solid **14**: NMR ($CDCl_3$) δ 1.8 (m, 6 H), 2.1 (d, ^4J = 3 Hz, 1 H), 2.5 (s, 3 H), 2.8 (m, 1 H, propargyl), 4.9 (m, 1 H, CHOTs), 7.65 (approx. dd, 4 H);

(38) Crandall, J. K.; Lin, L.-H. C. *J. Org. Chem.* **1968**, *33*, 2375.

(39) Shriver, D. G. "The Manipulation of Air Sensitive Compounds"; McGraw-Hill: New York, 1969.

(40) The positions of the methyl resonance and of the signals due to coordinated ether correspond to those expected in view of the data reported for methyl aluminum chloride etherates: Mole, T. *Aust. J. Chem.* **1964**, *17*, 1050.

(41) Fieser, L. F.; Fieser, M. "Reagents for Organic Synthesis"; Wiley: New York, 1967; p 1179.

IR (Nujol) 3270, 2115, 1178, 1190 cm^{-1}.

***cis*-2-Ethynylcyclopentyl Formate (15).** Both 7.3 g (28 mmol) of **14** and 35 g (190 mmol) of benzyltrimethylammonium formate (prepared from Aldrich Triton-B solution and formic acid, azeotropically dried with benzene) were dissolved in 350 mL of acetonitrile, and the mixture was refluxed 5 h under N_2, cooled, and reduced in volume in vacuo. Water (200 mL) was added, and the mixture was extracted with 3 × 75 mL of ether, which was washed with water and saturated NaCl and dried over anhydrous $MgSO_4$. Rotary evaporation gave 3.2 g (23 mmol, 84%) of crude **15**, of which 0.25 mL was microdistilled (bp 25 °C (0.01 mm)) for spectroscopy and analysis. Gas chromatography (columns B and C) showed the product to be approximately 93% **15**; 3% appeared to be the trans isomer of **15** and an unknown impurity was about 4 area%: NMR ($CDCl_3$) δ 1.8 (m, 6 H), 2.1 (d, ^4J = 3 Hz, 1 H), 2.8 (m, 1 H), 5.4 (m, 1 H), 8.2 (s, 1 H); IR (neat) 3285, 2960, 2875, 2115, 1720, 1180, 1145 cm^{-1}. Anal. ($C_8H_{10}O_2$): C, H.

***cis*-2-Ethynylcyclopentanol (5c).** A mixture of 0.30 g of anhydrous K_2CO_3, 25 mL of absolute methanol, and 2.96 g (21.5 mmol) of crude **15** was stirred under N_2 for 45 min at 25 °C. The supernatant was decanted into 100 mL of ether, which was extracted with 2 × 100 mL of H_2O, which was back-extracted with 100 mL of ether. The combined ether solution was dried ($MgSO_4$), and solvent was distilled away at 1 atm. The residue was vacuum distilled, giving 1.63 g (69%) of **5c**; bp 68 °C (18 mm). GLC analysis (column B) showed this to be 97% pure. The NMR and IR spectra were virtually identical with reported spectra.[28] The low yield is largely due to volatility losses during solvent removal and distillation.

***cis*-4-Methylene-2-oxabicyclo[3.3.0]octan-3-one (6c).** Into the standard cyclocarbonylation apparatus were placed 0.081 g (0.459 mmol) of $PdCl_2$, 0.088 g (0.461 mmol) of anhydrous $SnCl_2$, 0.241 g (0.918 mmol) of $(C_6H_5)_3P$, and 50 mL of acetonitrile. This solution was carbonylated at 65 °C and 70 psi of CO for 1 h, and 0.494 g (4.40 mmol) of **5c** was then added via syringe. GLC showed complete reaction after 1.5 h, whereupon the solution was filtered through celite and solvent removed in vacuo. The addition of ether precipitated a red gum. The supernatant was chromatographed through a 7 in. by 0.5 in. Florisil column with ether eluant and concentrated in vacuo to a yellow oil. The product **6c** and an isomer were isolated by PTLC (silica gel, 5% ethyl acetate in benzene, R_f 0.55 and 0.26, respectively). The product **6c** was microdistilled (bp 35 °C (0.008 mm)) and shown to be 99% pure by GLC (column B). The IR and NMR spectra of **6c** were identical with those of authentic material prepared by the method of Roberts:[7a,42] ^1H NMR ($CDCl_3$) δ 6.2 (d, J = 3 Hz, 1 H), 5.65 (d, J = 2 Hz, 1 H), 4.9 (m, 1 H, CHO), 3.45 (m, 1 H, ring), 2.5–2.2 (m, 1 H, probably allylic), 2.2–1.4 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 170.64 (C=O), 140.21 (H_2C=*C*), 122.17 (H_2C=C), 82.97 (HCO), 42.75 (HCC=CH_2), 35.35, 33.58, 22.84; IR (neat) 2975, 2880, 1765, 1662, 1381, 1267, 1203, 1150, 1112, 985 cm^{-1}. The minor isomer from PTLC was identified as the dihydropyrone isomer of **6c**, *cis*-2-oxabicyclo[4.3.0]non-4-en-3-one, by comparison with reported IR and ^1H NMR spectra.[43]

Repetition with an internal standard gave a 93% GLC yield (column C) of **6c** and a 7% yield of its dihydropyrone isomer.

***trans*-4-Methylene-2-oxabicyclo[3.3.0]octan-3-one (4c).** Into a standard cyclocarbonylation apparatus were placed 0.806 g (4.55 mmol) of $PdCl_2$, 0.865 g (4.56 mmol) of anhydrous $SnCl_2$, 2.39 g (9.10 mmol) of $(C_6H_5)_3P$, and 300 mL of acetonitrile. The solution was carbonylated at 65 °C, 70 psi of CO, for several h, 5.02 g (45.6 mmol) of **3c** was introduced, and carbonylation was continued for 12 h. The solution was reduced to 10 mL in vacuo, 200 mL of ether and 60 mL of pentane were added, and the solution was cooled with dry ice, precipitating a red gum. The supernatant was filtered through celite, evaporated in vacuo, taken up in 5 mL of CH_2Cl_2, and added to 100 mL of ether at −78 °C, again precipitating a red gum. The supernatant liquid was filtered and evaporated to give 6.2 g of orange oil. The oil was then chromatographed in two parts through $^1/_2$ in. × 10 in. Florisil columns, eluting with 10% ether/CH_2Cl_2. Collected fractions were assayed by GLC (column C), combined, evaporated in vacuo, and microdistilled (0.01 mm, pot temperature 70–90 °C), giving a white crystalline solid, mp 35–39 °C. Alternatively, **4c** can be isolated by PTLC on silica gel using 5% ethyl acetate in benzene (R_f 0.55): ^1H NMR ($CDCl_3$) δ 6.05 (d, J = 3 Hz, 1 H), 5.45 (d, J = 4 Hz, 1 H), 3.7 (m, 1 H, CHO), 2.6 (m, 1 H, ring), 2.4–1.2 (m, 6 H, allylic and 5 ring H's); ^{13}C NMR ($CDCl_3$) δ 173.47 (C=O), 139.20 (H_2C=*C*), 116.16 (H_2C=C), 84.44 (HCO), 52.33 (HCC)=CH_2), 25.53, 23.11, 19.40; IR (neat) 2990, 2900, 1785, 1678, 1395, 1248, 1221, 1145, 1130, 1045, 1000, 692 cm^{-1}. Anal. ($C_8H_{10}O_2$): C, H. Repetition with an internal standard gave a 27% GLC yield after 21 h (column C). GLC also showed a 5% yield of the *cis*-**6c**, presumably arising from a small amount of the cis alcohol **5c** in the substrate trans alcohol **3c**.

Isomerization of 4c to 4-Methyl-2-oxabicyclo[3.3.0]oct-4-en-3-one (22). To 1.11 g (1.21 mmol) of $[(C_6H_5)_3P]_3RhH(CO)$[35] under N_2 was added by syringe 25 mL of 1,4-dioxane and 0.330 g (2.39 mmol) of **4c**. The solution was stirred 1.5 h at room temperature and was monitored by GLC (column C). Dioxane was then removed in vacuo, and 30 mL of ether was added giving a slurry of yellow solid which was filtered through celite and washed with 2 × 10 mL of ether. The filtrate was evaporated in vacuo, taken up in 5 mL of ether, and refrigerated overnight to give another crop of yellow crystals. To this was added 10 mL more of ether, of the slurry was again filtered, and the ether was removed leaving a red oil. From this **22** was isolated by PTLC (silica gel, 5% ethyl acetate in benzene, R_f 0.4) and distilled bulb to bulb at 0.02 mm (pot temperature 60 °C) giving 0.204 g (1.48 mmol, 62% yield) of the known butenolide:[7a] ^1H NMR ($CDCl_3$) δ 4.67 (m, 1 H, CHO), 2.24 (approximately dd, 2 H), 1.97 (m, 3 H), 1.56 (d, ^5J = 2 Hz, 3 H), 1.1 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 175.5, 169.5, 119.4, 82.8 (CHO), 28.8, 23.3, 20.8, 8.63; IR (neat) 2940, 2895, 1765, 1705, 1092, 1060 cm^{-1}.

Isomerization of 6c to 22. In a similar fashion, 37.8 mg (0.274 mmol) of **6c** was isomerized by 120 mg (0.130 mmol) of $[(C_6H_5)_3P]_3RhH(CO)$ in 2.7 mL of 1,4-dioxane for 1.5 h. The major product was not isolated but was shown to be identical with isolated **22** by GLC coinjection (columns C and D) and by TLC.

α-Methylene-δ-valerolactone (17). In the usual apparatus 4-pentyn-1-ol, **16** (0.36 g, 4.3 mmol), was added to a solution of $PdCl_2$ (0.012 g, 0.07 mmol), anhydrous $SnCl_2$ (0.013 g, 0.07 mmol), PPh_3 (0.037 g, 0.14 mmol), and naphthalene (0.229 g, 0.23 mmol) in 15 mL of CH_3CN at 76 °C and stirred under 80 psi of CO for 16 h. GLC analysis of the reaction solution indicated a yield of 0.247 g (2.2 mmol, 51%) of the known α-methylene-δ-valerolactone **17**. The IR and NMR spectra of a sample isolated by preparative GLC agreed with those reported.[4h]

Cyclocarbonylation of 1-Bromohex-5-yn-3-ol, 10, to 18. In the usual apparatus **10** (0.76 g, 4.3 mmol) was added to a solution of $PdCl_2$ (0.034, g, 0.19 mmol), anhydrous $SnCl_2$ (0.036 g, 0.19 mmol), and PPh_3 (0.100 g, 0.38 mmol in 15 mL of acetonitrile at 75 °C and stirred under 100 psi of CO. The reaction solution was reduced in volume by rotary evaporation, diluted with 150 mL of ether, and passed through a 5 in. × 1 in. Florisil column. Removal of ether yielded 0.74 g of a yellow oil, a sample of which (0.46 g) was placed in an NMR tube with a weighed amount of benzene. Integration of the NMR indicated a 70% yield of **18**: NMR (C_6D_6) δ 1.6–3.0 (m, 4 H), 3.22 (t, ^3J = 6 Hz, CH_2Br), 4.32 (m, 1 H, CHO_2C), 5.33 (t, J = 2 Hz, 1 H, syn H), 5.91 (t, J = 2 Hz, 1 H, anti H); IR (CH_2Cl_2) 1760, 1665 cm^{-1}. Anal. ($C_7H_9O_2Br$): C, H, Br.

Cyclocarbonylation of Oct-7-en-1-yn-4-ol (12) to 19. A mixture consisting of 0.160 g (0.905 mmol) of $PdCl_2$, 0.172 g (0.906 mmol) of anhydrous $SnCl_2$, and 0.475 g (1.81 mmol) of $(C_6H_5)_3P$ in 30 mL of acetonitrile was carbonylated 1 h at 75 °C and 100 psi of CO. To this was added by syringe 0.449 g (3.62 mmol) of **12**, CO pressure was reapplied, and the reaction was monitored by GLC (column C) until ca. 90% of **12** was consumed (4.5 h). The solution was then quickly cooled, filtered through celite, and reduced to 3-mL volume in vacuo. Ether (10 mL) was added, and the solution was chromatographed through a 15 × 3 cm Florisil column with ether eluant. The product was isolated by PTLC (silica gel, 5% ethyl acetate in benzene, R_f = 0.50), and purified by bulb to bulb distillation (0.005 mm with pot temperature 60 °C): NMR ($CDCl_3$, 360 MHz) δ 6.22 (t, J = 3.3 Hz, 1 H, α-C=CH_2), 5.82 (m, 1 H, vinyl CH), 5.64 (t, J = 2.4 Hz, 1 H, α-C=CH_2), 5.1–5.0 (m, 2 H, side chain vinyl CH_2), 4.55 (m, 1 H, HCO), 3.08 (m, 1 H, ring allyl), 2.61 (m, 1 H, ring allyl), 2.22 (m, 2 H, side chain allyl), 1.9–1.6 (m, 2 H, side chain homoallyl); IR (neat) 2965, 2925, 2840, 1755, 1655, 1633 cm^{-1}. Anal. ($C_9H_{12}O_2$): C, H. Repetition of this reaction with an internal standard and GLC monitoring (column C) showed that when 89% of **12** had been consumed, **19** had been formed in 43% yield. Further reaction decreased the yield of **19** with concommitant formation of unidentified secondary products.

Cyclocarbonylation of 3-buten-1-ol (20) to α-Methylbutyrolactone (21) and δ-Valerolactone. A mixture containing 0.064 g (0.358 mmol) of $PdCl_2$, 0.068 g (0.358 mmol) of anhydrous $SnCl_2$, and 0.189 g (0.719 mmol) of $(C_6H_5)_3P$ in 5 mL of acetonitrile was carbonylated at 90 °C, 100 psi of CO, for 2 h. Then 0.661 g (5.50 mmol) of mesitylene internal standard and 0.570 g (7.90 mmol) of **20** were added by syringe, and pressure was reapplied. After 18.5 h analysis showed 75% consumption of **20**, a 26% yield of **21**, and a 14% yield of a side product identified as δ-valerolactone by coinjection with a commercial sample (columns C and D).

(42) We found that 4-*exo*-bromo-4-*endo*-methyl-2-oxabicyclo[3.3.0]octan-3-one could be selectively dehydrobrominated to **6c** by DBN from a mixture of the 4-*exo*-bromo and 4-*endo*-bromo isomers.

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Competitive Cyclocarbonylation of 5c and 3c. A mixture consisting of 0.022 g (0.122 mmol) of $PdCl_2$, 0.024 g (0.128 mmol) of anhydrous $SnCl_2$, 0.065 g (0.246 mmol) of $(C_6H_5)_3P$, and 0.138 g (1.08 mmol) of naphthalene internal standard in 15 mL of acetonitrile was stirred 1.5 h at 65 °C under 70 psi of CO. To this was added 0.117 g (1.06 mmol) of **5c** and 0.165 g (1.50 mmol) of **3c**, and the CO pressure was restored. Aliquots were periodically analyzed by GLC (column C). Relative rates $k_{obsd}(cis)/k_{obsd}(trans)$ were obtained from

$$\frac{k_{obsd}(cis)}{k_{obsd}(trans)} = \frac{\Delta 5c/[5c]_{t=0}}{\Delta 3c/[3c]_{t=0}} = \frac{(\%\text{ yield of trans})\Delta 6c/[5c]_{t=0}}{(\%\text{ yield of cis})\Delta 4c/[3c]_{t=0}}$$

over four time intervals within the first 3 h of reaction; $k_{obsd}(cis)/k_{obsd}(trans) = 1.01 \pm 0.10$ from eight determinations. After 5 h the yield of *cis*-**6c** was 63% and that of *trans*-**4c** 32%.

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Anionic Metal Hydride Catalysts. 1. Synthesis of Potassium Hydrido(phosphine)ruthenate Complexes

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Abstract: The potassium hydrido(phosphine)ruthenate complexes $K^+[(Ph_3P)_2Ph_2\overline{PC_6H_4RuH_2}]^-\cdot C_{10}H_8\cdot(C_2H_5)_2O$ (**1**) and $K_2^+[(Ph_3P)_3(Ph_2P)Ru_2H_4]^{2-}\cdot 2C_6H_{14}O_3$ (**2**) were prepared for study as possible homogeneous catalysts for the catalytic hydrogenation of polar organic substrates. Complex **1** was prepared by reaction of $(Ph_3P)_3RuHCl\cdot C_6H_5CH_3$ (1 mol) with potassium naphthalene (2 mol) at −80 to −111 °C in tetrahydrofuran (THF). It was isolated as a yellow crystalline solid from solutions in diethyl ether and in the presence of excess naphthalene ($C_{10}H_8$). The complex was characterized by a combination of chemical and spectral techniques and single-crystal X-ray crystallography. The complex crystallizes in space group $P\bar{1}$ with $a = 15.603$ (6) Å, $b = 15.974$ (4) Å, $c = 23.774$ (8) Å, $\alpha = 90.69$ (2)°, $\beta = 102.96$ (3)°, $\gamma = 106.51$ (3)°, and contains four formula units of **1** in the unit cell. In the asymmetric unit there are two different molecules of **1**: consisting of two $[(Ph_3P)_2Ph_2\overline{PC_6H_4RuH_2}]^-$, ruthenate anions, associated potassium (counterions), and also diethyl ether and naphthalene as molecules of crystallization. In the ruthenate anions there is a distorted octahedral arrangement of two triphenylphosphine and one ortho-metalated triphenylphosphine ligands around ruthenium. Two hydride atoms (not located by the crystallography) are assumed to occupy the remaining pseudooctahedral positions. The presence of the hydride atoms was shown by infrared spectra (ν_{Ru-H} = 1735, 1825 cm^{-1}), ^1H NMR spectra ($\delta_{(CH_3)_4Si} = -7, -11$), and the reactions of **1** with HCl and CH_3I to give respectively H_2 (2.0 mol/mol of **1**) and CH_4 (2.4 mol/mol of **1**)). The second hydrido(phosphine)ruthenate complex **2** was prepared by the analogous potassium naphthalene reduction of $[(Ph_3P)_2RuHCl]_2\cdot 2$toluene. The composition of **2** as obtained by crystallization from toluene/diglyme ($C_6H_{14}O_3$) was established from ^1H and ^{31}P NMR spectra and its chemical reactivity with HCl to yield H_2 (~2 mol/mol of Ru) and a tris(triphenylphosphine)(diphenylphosphine)diruthenium chloride complex.

In recent years a wide variety of homogeneous catalysts have been developed for the hydrogenation of organic substrates.[1c] The transition-metal phosphine complexes, for example, $(Ph_3P)_3RhCl$, $(Ph_3P)_3RuHCl$,[2] $[Ir(COD)(PMePh_2)_2]PF_6$[3] are highly effective catalysts for the hydrogenation of olefins to alkanes. In contrast there are relatively few homogeneous catalysts for the hydrogenation of polar unsaturated compounds such as aldehydes, ketones, and nitriles.[4]

In this work we sought to prepare a class of soluble metal catalysts which would be widely applicable to the hydrogenation of polar organic functional groups. Main-group metal hydrides (e.g., $LiAlH_4$ and various borohydrides) are widely used for the stoichiometric reduction of ketones, nitriles, etc.[5] We felt that certain formally analogous, anionic transition-metal hydride complexes of formula $A^+[L_nM-H_x]^-$ might be prepared which could act as catalytic hydride-transfer agents, the overall reduction being effected by hydrogen gas in equilibrium with the complex. To this end we attempted the synthesis of several such hydridometalate complexes wherein A^+ is an alkali-metal cation, M is a group 8 metal, and L a tertiary phosphine ligand.

Transition-metal hydride complexes can range from predominantly acidic ($L_nM^{\delta-}-H^{\delta+}$) to hydridic ($L_nM^{\delta+}-H^{\delta-}$) in character, depending on the nature of the metal atom and the charge-transfer characteristics of the complementary ligands.[6] The anionic

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