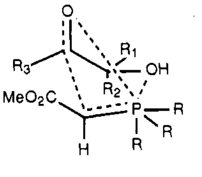
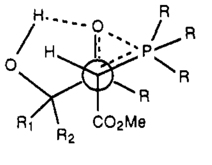
stage be premature, the following two transition-state models may be useful in rationalizing our results. The first involves initial interaction of an α-hydroxyl group with the phosphorus center of the ylide. This would permit the ylide to add to the carbonyl by way of a *bicyclic* transition state A that minimizes axial substituents as shown. Once C–C bond formation has occurred, syn elimination of Ph$_3$PO in the usual way would afford the observed E olefin. Alternatively, the carbonyl might first be activated by an intramolecular hydrogen bond followed by a concerted cycloaddition of the ylide.[12] In this case the transition-state B (parallel *or* tilted approach of ylide) requires that the large phosphorous ligands approach the conformationally mobile α'-carbon and would explain why the rate of reaction is most sensitive to substitution at this position. As with the previous model, transition-state B leads to a *trans*-oxaphosphetane, which then decomposes to give the observed E-olefinic product.



A



B

In light of continued interest in the synthesis and use of functionalized olefins in general, we feel that the described procedure provides a valuable addition to already established methodology. Further studies to delineate the scope and mechanism of this potentially useful hydroxyl-directed Wittig reaction are currently under way.

Acknowledgment. This work was supported by Public Health Service Research Grant GM 35557 from the National Institute of General Medical Sciences and a Case Institute of Technology BRSG Award.

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(12) *Intermolecular* acid catalysis of the Wittig reaction between stabilized ylides and ketones is known: Ruecchardt, Ch.; Eichler, S.; Panse, P. *Angew. Chem.* 1963, *75*, 858.

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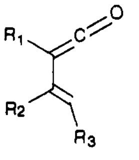
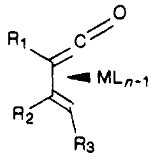
Practical Organic Synthesis with Strained-Ring Molecules. Rhodium-Catalyzed Carbonylation of Cyclopropenyl Esters and Cyclopropenyl Ketones to α-Pyrones and of Vinyl Cyclopropenes to Phenols[1a]

Summary: Cyclopropenyl esters, prepared from alkynes and ethyl diazoacetate via rhodium acetate catalysis, can be converted into cyclopropenyl ketones, which in turn are converted into vinyl cyclopropenes. All three classes of cyclopropenes undergo rhodium-catalyzed carbonylation at 1 atm of CO to provide α-pyrones from the first two classes and phenols from the last.

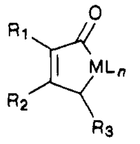
Sir: Vinylketenes **1**, generated by the ring opening of cyclobutenones or via eliminations from unsaturated carboxylic acid derivatives, have proven to be useful intermediates in organic synthesis,[2] and during the last few years vinylketene metal complexes **2a–c** have been implicated in reactions of transition-metal carbenes with alkynes which also produce useful organic products.[3]



1



η^4-vinylketene
2a



η^2-vinylketene
2b

Another procedure known to produce vinylketene–metal complexes is the reaction of cyclopropenes with stoichiometric metal carbonyl reagents.[4] We have developed an interest in synthetically useful metal-catalyzed chemistry of strained-ring organic molecules and were led to consider the possibility of the metal-catalyzed carbonylation of cyclopropenes as a route into vinylketene intermediates with synthetic organic potential. Specifically, we were interested in the metal-catalyzed carbonylation of cyclopropenyl esters and ketones **3**, X = O, and vinylcyclopropenes **3**, X = CHR$_4$, as a route to α-pyrones and phenols, respectively, as shown in Scheme I. Relevant reactions of cyclopropenes with transition metals can be found in the work of Semmelhack,[5] Binger,[6] Hughes,[7,8] and others.[4,9]

While many cyclopropenes cannot be categorized as attractive starting materials for the synthesis of organic

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(1) (a) This work was presented at the 192nd National Meeting of the American Chemical Society, Anaheim, CA, Sept. 7–12, 1986. (b) Fellow of the Alfred P. Sloan Foundation, 1983–1987; Camille and Henry Dreyfus Teacher Scholar, 1986–1991.

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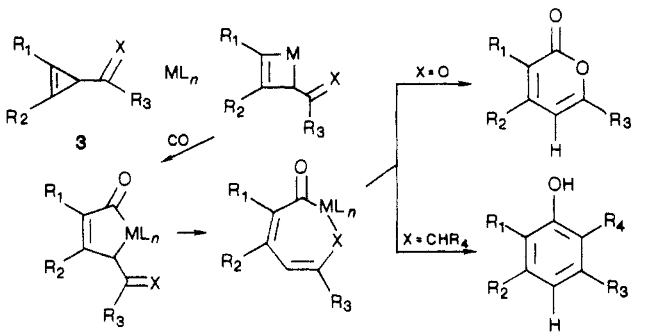
0022-3263/87/1952-2631$01.50/0

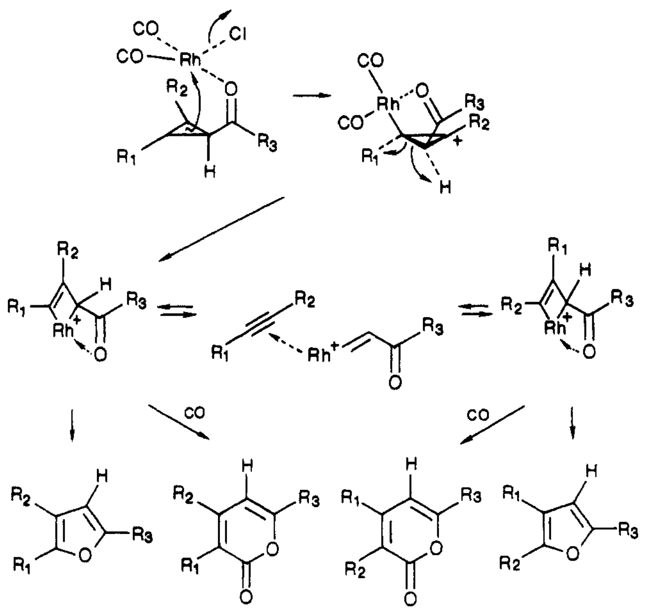
Scheme I



molecules, cyclopropenyl esters are readily available by the slow addition at room temperature of ethyl diazoacetate to neat alkynes containing 1.2 mol % rhodium acetate as catalyst.[10] Cyclopropenyl esters were found to be excellent starting materials for the preparation of cyclopropenyl ketones through the use of the Weinreb ketone synthesis.[11] The cyclopropenyl ketones, in turn, reacted with phosphorus ylides or via the Takai olefination protocol[12] to provide a variety of substituted vinyl cyclopropenes in moderate to good yields.[13]

Having a flexible synthetic route to these molecules, the metal-catalyzed carbonylation sequence depicted in Scheme I was studied. Catalytic carbonylation of the cyclopropenes was performed by using 2 mol % of $[ClRh(CO)_2]_2$ and 1 atm of CO in noncoordinating solvents such as benzene and cyclohexane. A multitude of products was formed when $Pd(PPh_3)_4$ was used as catalyst. Results of the carbonylation of a variety of cyclopropenyl esters

Scheme II



and ketones are described in Table I. From the results listed in the table, a number of trends are noted. Most obvious is the pronounced regioselectivity observed in the α-pyrone formation. Cyclopropenyl esters derived from terminal alkynes cleanly produced the 4-substituted isomer of the pyrone; the same product was formed after desilylation of the pyrone formed by carbonylation of the trimethylsilyl-substituted cyclopropenyl ester.[14] Carbonylation of the cyclopropenyl ketones proceeded with facility equal to the cyclopropenyl esters; however, in the former case there was a pronounced tendency to form furans[15] in addition to the expected pyrones. Better selectivity for the synthesis of the pyrone product might be achieved at higher CO pressures, and significant improvement in the pyrone–furan ratio was observed at elevated CO pressure. Treatment of 1-benzoyl-2,3-diethylcyclopropene with 1000 psi CO and 2 mol % $[ClRh(CO)_2]_2$ at room temperature over 2 days led to the isolation of 85% pyrone and 12% furan in contrast to a control reaction at room temperature and 1 atm of CO that gave 67% pyrone and 30% furan or to the 80 °C reaction results shown in entry 7 of Table I. Of particular interest was the observation that the pyrones formed from the cyclopropenyl ketones derived from terminal alkynes were exclusively the 3,6-substituted isomers, in distinct contrast to the 4,6-substituted isomers formed from the cyclopropenyl esters.

The efficient formation of α-pyrones from cyclopropenyl esters and ketones suggested that vinyl cyclopropenes would readily carbonylate and form phenols. In a few preliminary reactions, vinyl cyclopropenes, prepared by olefination of the cyclopropenyl ketones, were treated with catalytic $[ClRh(CO)_2]_2$ under 1 atm of CO at 80 °C (entries 14–17, Table I). As anticipated, these reaction conditions

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(5) During the course of our investigation of the carbonylation of cyclopropenes, we became aware of similar chemistry being pursued in the Semmelhack laboratory: *Abstracts of Papers*, 192nd National Meeting of the American Chemical Society, Anaheim, CA; American Chemical Society: Washington, dC, 1986; ORGN 130.

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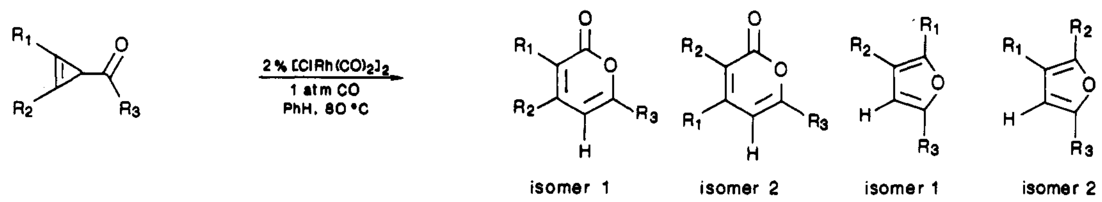
(13) All new compounds gave satisfactory elemental analyses or high-resolution mass spectra in addition to showing IR and high-field NMR spectra consistent with the assigned structures.

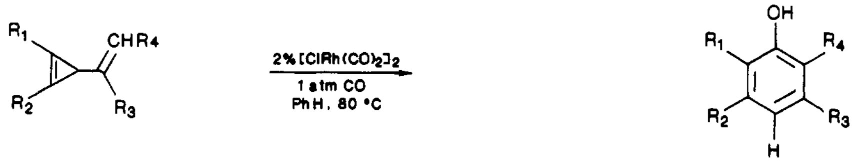
(14) Analysis of the reaction product before desilylation suggested the formation of a 50/50 mixture of 6-ethoxy-4-methyl-3-(trimethylsilyl)-2-pyrone and 6-ethoxy-4-methyl-5-(trimethylsilyl)-2-pyrone. This same "scrambling" of products was also observed in the carbonylation of 1-carbethoxy-2-*n*-butyl-3-deuteriocyclo-2-propene, but the scrambling process is restricted to the case of cyclopropenyl esters since attempts to observe similar product mixtures in the cyclopropenyl ketones were unsuccessful. This curious reaction is probably related to a pyrone iron tricarbonyl complex equilibration previously documented by Semmelhack.[3j] We will describe our studies of this process in more detail in a full paper.

(15) Cyclopropenyl esters are known to rearrange thermally to furans in the presence of a copper catalyst (Komendantov, M. I.; Domnin, I. N.; Bulucheva, E. V. *Tetrahedron* **1975**, *31*, 2495).

Table I. Rhodium-Catalyzed Carbonylation of Cyclopropenes. A Synthesis of α-Pyrones and Phenols[13]



					pyrone yields,[b] %		furan yields, %	
entry	R_1	R_2	R_3	cyclopropene,[a] %	isomer 1	isomer 2	isomer 1	isomer 2
1	Et	Et	OEt	78	78			
2	H	n-Bu	OEt	86	77			
3	H	t-Bu	OEt	59	89			
4	H	$(CH_2)_3Cl$	OEt	97	72			
5	Me	Ph	OEt	93	60[c]	26	9	
6	$SiMe_3$	Me	OEt	71	77 (R_1 = H)[d]			
7	Et	Et	Ph	81	40		52	
8	Et	Et	Me	37	47			
9	Et	Et	$CH{=}CH_2$	54	45		25	
10	Et	Et	$C{\equiv}CPh$	95	48		52	
11	H	n-Bu	Ph	48		62		28
12	D	n-Bu	Ph	58		48		27
13	H	n-Bu	Me	64		25		



	R_1	R_2	R_3	R_4	vinylcyclopropene yield, %	phenol yield, %
14	Et	Et	Ph	H	80	31
15	Et	Et	Ph	Ph	42	51
16	Et	Et	Ph	n-Pr	40	82
17	Et	Et	i-Pr	H	48	46

[a] The cyclopropenyl esters of entries 1–6 were prepared according to the method of ref 10. The method of Weinreb[11] was used to prepare the cyclopropenyl ketones (entries 7–13) from the esters. The required cyclopropenyl acid chlorides were prepared from the cyclopropenyl esters following the procedure described in: Hughes, R.; Donaldson, W. *J. Am. Chem. Soc.* **1982**, *104*, 4846. [b] Identified through use of the chemical shift and coupling constants of the α-pyrone olefinic hydrogens. The parent 6-methoxy-2-pyrone showed the following absorptions: H α to CO, δ 5.86; H β to CO, δ 7.39; H γ to CO, δ 5.37 (Mitsudo, T.; Ogino, Y.; Watanabe, H.; Watanabe, Y. *Organometallics* **1983**, *2*, 1202. Similar chemical shifts are observed in other 6-methoxy-α-pyrones (Jung, M.; Brown, R. *Tetrahedron Lett.* **1982**, 3355. Jung, M.; Lowe, J. *J. Chem. Soc., Chem. Commun.* **1978**, 95). In every case investigated, the α-pyrones formed from the cyclopropenyl esters showed vinyl hydrogen absorptions near δ 5.2. Similar spectroscopic trends were used to determine the structures of the pyrones produced from the cyclopropenyl ketones. [c] Major and minor isomers were identified by NOE. Irradiation at the CH_3 group absorption in the *minor* isomer caused enhancement of the olefinic absorption at δ 5.3, while the major isomer showed no NOE enhancement of the vinyl hydrogen signal in a similar experiment. [d] Desilylation was performed by treatment of the silylated pyrone with excess 1 M $n\text{-}Bu_4N^+F^-$ in THF at 0 °C for 30 min. [e] Prepared via the methylenation procedure of Takai.[12] [f] Prepared via standard Wittig procedures.

led to the efficient formation of substituted phenols, although significant amounts of cyclopentadienes were noted under these conditions. Ongoing studies will delineate the influence of CO pressure on the reaction as well as the regioselectivity of this phenol synthesis.

The accumulated observations on reactivity and regioselectivity in the α-pyrone synthesis suggested the overall reaction pathway shown in Scheme II. The formation of 4-substituted 6-ethoxy-2-pyrones from both the $SiMe_3$ and H-substituted cyclopropenyl esters of entries 2–4 and 6 in Table I dictates the regioselective breaking of the carbon–carbon bond of the cyclopropene bearing the COOEt and vinyl $SiMe_3$ and the COOEt and vinyl H, respectively, strongly implying that electronic effects and not steric effects dominate the regioselectivity of the α-pyrone synthesis. These results, together with the observation that an electron-withdrawing COOEt substituent on the cyclopropene double bond completely suppressed carbonylation, led us to propose electrophilic attack of $[ClRh(CO)_2]_2$ on the π-bond of the cyclopropene to afford the best stabilized cyclopropyl carbocation. Ring opening of the resulting cyclopropyl cation accounts for the regiochemistry of pyrone formation from the cyclopropenyl esters (Scheme II). All 6-ethoxy-2-pyrone isomers conform to this model. A complication arises when considering the structure of the 2-pyrones formed from the cyclopropenyl ketones derived from terminal alkynes (Table I, entries 11–13). In these cases carbonylation produced the 3,6-disubstituted 2-pyrones as evidenced by the vicinal nature of the pyrone olefinic hydrogens and their chemical shifts. It seems unlikely that the mechanism of carbonylation of cyclopropenyl esters should be fundamentally different from the mechanism of carbonylation of the cyclopropenyl ketones, so we considered the equilibration of metallacyclobutene intermediates shown in Scheme II.[16] To explain the observed products, we propose that the 1,3-disubstituted metallacyclobutene is more stable than the 1,2-disubstituted metallacyclobutene and that for the cyclopropenyl ketones, but not the cyclopropenyl esters, metallacycle equilibration is faster than carbonylation of

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[16] Ring opening of metallacyclobutenes is precedented: Tebbe, F. N.; Harlow, R. L. *J. Am. Chem. Soc.* **1980**, *102*, 6151.

the metallacycle to the α-pyrone. This proposal allows rationalization of the peculiar change in product regiochemistry when changing from the cyclopropenyl esters to the cyclopropenyl ketones. Furthermore, it suggests that higher CO pressures could minimize the metallacyclobutene equilibration seen in entries 11–13 of Table I. Carbonylation of 1-*n*-butyl-3-benzoylcyclopropene at 1000 psi of CO at room temperature for 2 days in cyclohexane did significantly minimize furan formation; however, the 3,6-disubstituted pyrone was still the only isomer isolated (60% pyrone and <1% furan were obtained). Additional studies are currently under way to improve the synthetic potential of the catalytic carbonylation of cyclopropenes and to further probe the intriguing mechanistic questions raised by this study.

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