of increasing electron demand to detect the onset of σ bridging in 2-aryl-2-norbornyl system **15** and related systems **16** and **18** with substituents more electron demanding than phenyl. We have also shown that in some cases with similar deviations the origin of such effects may be entirely different. Judicious application of the Gassman–Fentiman tool of increasing electron demand coupled with ^{13}C NMR spectroscopy as the structural probe is useful to determine the onset of π, $\pi\sigma$, or σ delocalization provided alternative explanations for the data are ruled out. No claim was ever made by the originators that the method was selective for σ delocalization. However, it should be reemphasized that, since phenyl groups even with electron-withdrawing substituents can still delocalize charge into the π system, the method is not sensitive enough to detect bridging in cases where structural changes are limited, including systems which are partially bridged or delocalized. For the same reasons the method must be considered ineffective in may solvolytic studies, since solvation significantly masks the electron demand of the cationic center in the solvolytic transition state unless the structural change is significant (as in the case of the 7-norbornenyl, 5-norbornen-2-yl, or pentacyclononyl systems).

We make no sweeping new claims for the Gassman–Fentiman tool of increasing electron demand. Nonetheless, in the midst of the polemics, the clear fact remains that the norbornyl cation, when probed with this tool, responds in a way qualitatively different from a large number of normal cations. That difference begs to be explained and is uniquely consistent with the onset of σ bridging. Until a definitive experiment appears which is inconsistent with that interpretation or an acceptable alternate explanation appears which is consistent with all the facts we see no reason to alter our conclusion.

We are therefore amused to read Brown's concluding statement[2] "We have now shown that such deviations are not diagnostic of nonclassical σ bridging. Thus this criterion must join the huge graveyard of disproved criteria for nonclassical structures." It seems to us that this criterion, along with many others "laid to rest" by Brown, will, like Lazarus, refuse to accept this premature consignment to the tomb.

Mercury in Organic Chemistry. 24.[1] Mercuration and Subsequent Carbonylation of 4-Hydroxy-2-alkyn-1-ones: A Novel Route to Furans

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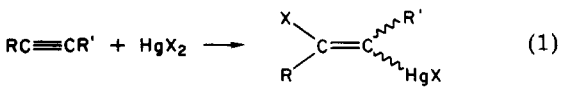
Mercuric chloride readily adds to the carbon–carbon triple bond of certain 4-hydroxy-2-alkyn-1-ones (**3a**, **3b**, and **3e**) to give vinylmercurials which appear to be the first syn addition compounds of mercuric chloride. These vinylmercurials readily dehydrate to 3-furylmercurials. Palladium-promoted carbonylation of these compounds affords 3-furyl carbonyl compounds.

Mercury(II) salts are known to readily add to a variety of acetylenes to afford vinylmercurials (eq 1). Thus,



(1)

X = F, Cl, OAc, SCN

mercuric halides are reported to add to acetylene (anti),[2-7] propyne (anti),[8] cyclooctyne,[9] vinylacetylene (anti?),[8,10-12] alkynyl ethers,[13-15] propargylic alcohols (anti)[16-18] and halides (anti),[16,19] and α,β-unsaturated ketones,[20] acids (anti),[21-23] and esters (anti?)[21,24,25] with the stereochemistry

(1) Part 23: Larock, R. C.; Takagi, K.; Hershberger, S. S.; Mitchell, M. A. *Tetrahedron Lett.* **1981**, 5231.
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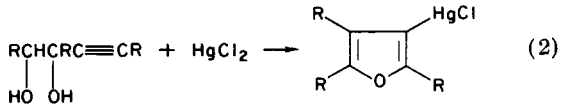
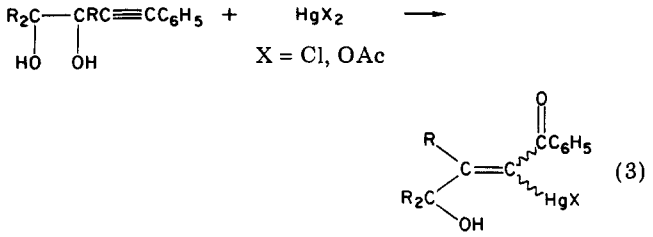
indicated. While the stereochemistry of addition has not always been determined, there appear to be no examples of mercuric halides adding to acetylenes in a syn fashion. Mercuric chloride also adds to certain acetylenic diols to afford furylmercurials (eq 2).[26-32] On the other hand,



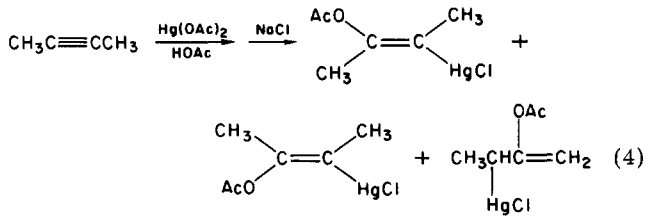
(2)

phenyl-substituted acetylenic tertiary diols react with mercuric chloride and mercuric acetate to give vinylmercurials (eq 3).[33-35]



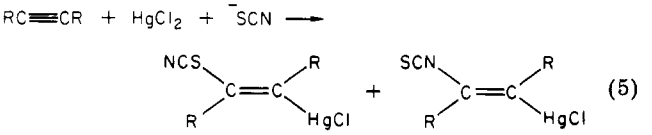
(3)

The reaction of acetylenes and mercuric acetate in acetic acid is reported to generate several different types of addition compounds. Terminal alkynes generally give dialkynylmercurials.[36-38] Simple internal aliphatic acetylenes appear to afford both regio- and stereochemical mixtures of vinylmercurials with anti adducts predominating,[39-42] as illustrated by the reaction of 2-butyne (eq 4),[43-45] while arylalkylacetylenes yield regiochemical mixtures of exclusively anti adducts.[37,46,47] Diphenylacetylene affords both syn and anti addition compounds, but in this case the former predominates.[43,45,46,48]



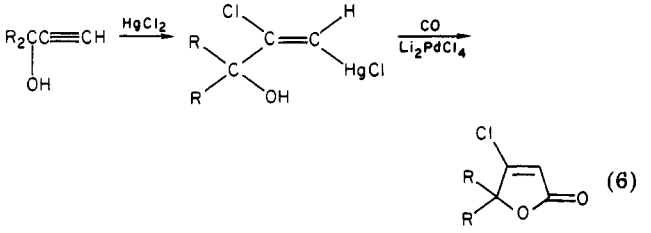
(4)

Recently, mercuric chloride and thiocyanide anion have been reported to add to internal acetylenes to give both sulfur- and nitrogen-bonded anti addition compounds (eq 5).[49]

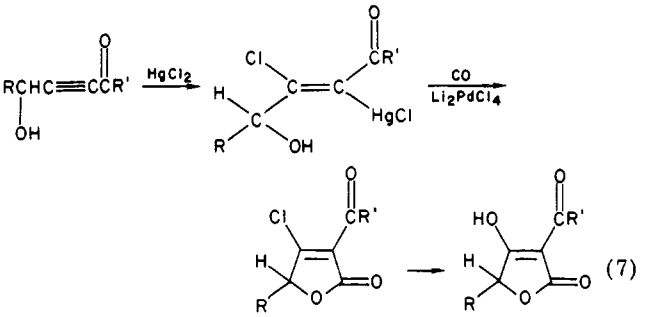


(5)

Our recent work on the mercuration and subsequent carbonylation of propargylic alcohols has provided a novel route to the butenolide ring system (eq 6).[17,18] In attempting to extend this approach to the synthesis of α-acyltetronic acids (eq 7), an important class of biologically active compounds,[50-61] we have examined the mercuration



(6)



(7)

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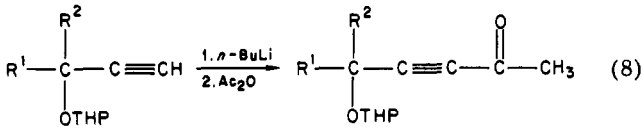
and subsequent carbonylation of 4-hydroxy-2-alkyn-1-ones. We wish to report here that the reaction of these acetylenes with mercuric chloride does not proceed as expected, but apparently affords the first example of the syn addition of mercuric chloride to an acetylene and provides a novel route to furylmercurials, which upon carbonylation afford furan-containing carbonyl compounds.

Results and Discussion

Preparation of 4-Hydroxy-2-alkyn-1-ones. Several 4-hydroxy-2-alkyn-1-ones were prepared by the method of Duranti and Balsamini[62] with only slight modification. The commercially available acetylenic alcohols propargyl alcohol, 1-butyn-3-ol, and 3-methyl-1-butyn-3-ol were protected as the corresponding tetrahydropyranyl (THP) ethers, deprotonated by *n*-butyllithium, and then reacted with excess acetic anhydride at −78 °C (eq 8). The desired

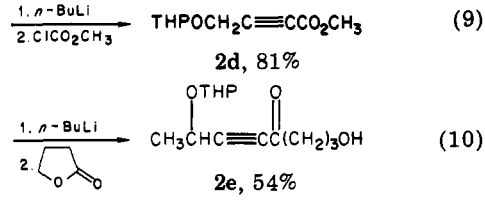


(8)

1a-c 2a-c

	R^1	R^2	isolated yield (%)
2a	H	H	54
2b	H	CH_3	61
2c	CH_3	CH_3	54

acetylenic ketones were obtained in modest yields, with 9–19% yields of recovered starting acetylenes. Since the corresponding 4-hydroxy-2-alkyn-1-ones are quite sensitive to light, heat, and air and can be stored for only short periods of time at −20 °C in the dark,[62] the THP derivatives were deprotected only immediately prior to mercuration. The acetylenic ester **2d** and ketone **2e** were prepared similarly (eq 9, 10). In the latter case, 25% of the



(9)

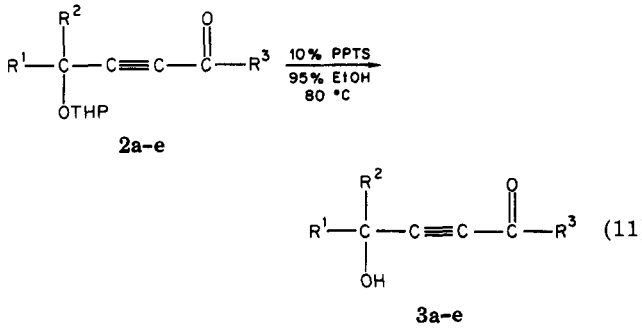
2d, 81%

(10)

2e, 54%

starting acetylene was recovered.[63,64]

The desired acetylenic alcohols can be obtained in almost quantitative yield by reacting the corresponding THP ethers with 10% pyridinium *p*-toluenesulfonate (PPTS) in 95% ethanol at 80 °C (eq 11).[65] The alcohols were



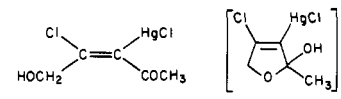
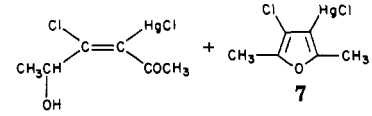
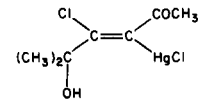
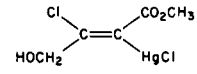
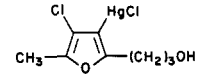
(11)

2a-e 3a-e

isolated by passage through a short silica gel column to remove PPTS, and they were then mercurated directly.

Mercuration of 4-Hydroxy-2-alkyn-1-ones. The 4-hydroxy-2-alkyn-1-ones dissolved in methanol were then treated in the dark at 0 °C for 10–12 h with an aqueous solution saturated with both mercuric chloride and sodium chloride. Simple filtration and a cold aqueous wash generally afforded high yields of a variety of interesting organomercurials, as summarized in Table I. The structures of the resulting products have been assigned on the basis of a variety of spectroscopic and analytical techniques as well as from the products resulting from their carbonylation.

Table I. Mercuration of 4-Hydroxy-2-alkyn-1-ones

4-hydroxy-2-alkyn-1-one	product(s)	% yield[a]
3a	 4 5	75 (30)[b]
3b	 6 7	90 (63)[c]
3c	 8	100 (72)
3d	 9	100 (72)
3e	 10	17 (13)

[a] Isolated yield (recrystallized yield). [b] After recrystallization, a small amount of **5** is formed. [c] The recrystallized product is **7** only.

The initial product from the mercuration of **3a** has been tentatively assigned structure **4**. While we were unable to obtain a correct elemental analysis for this compound, ^1H NMR spectroscopy suggested that it is one pure compound and not a mixture of isomers. The infrared spectrum shows a strong carbonyl absorption. An attempted ^{13}C NMR analysis of this compound dissolved in acetone-d_6 overnight, however, showed peaks assignable to compound **5** and a furylmercurial. Subsequent ^1H NMR analysis of this same sample confirms this assignment. After recrystallization the ^1H NMR peak assigned to the methylene group in **4** changes from a clean doublet (coupled to the OH triplet) to an overlapping singlet and doublet, which suggests to us that compound **4** has partially isomerized to the corresponding hemiketal **5**. The similar chemical shifts of these two peaks appear to rule out isomerization of an *E* isomer of **4** to the hemiketal **5**, since one might expect significantly different chemical shifts for the methylene groups in two such different compounds. The furylmercurial is not observed upon recrystallization. Unfortunately, neither **4** nor **5** can be isolated pure even after several recrystallizations. While the present evidence does not allow us to conclusively establish the stereochemistry of **4**, the apparent formation of a cyclic hemiketal and furyl mercurial and the furan-containing products obtained upon carbonylation (to be discussed later) are strongly suggestive of the *Z* isomer **4**, which is shown.

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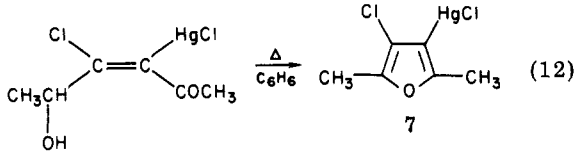
However, one cannot entirely rule out the possibility that compound **4** exists as the *E* isomer, which isomerizes during carbonylation.

The mercuration of **3b** proceeds in high yield to give a mixture of an acyclic vinylmercurial (**6**) and a furylmercurial (**7**) in a ratio of 95:5 as judged by ^{1}H NMR analysis. The ratio changes to 70:30 if the mercuration is run in 0.01 M HCl. Pure compound **6** can be obtained in low yield by very carefully recrystallizing the crude reaction mixture from benzene at low temperature and collecting only the first crystals formed. This compound gives a satisfactory elemental analysis and shows a strong carbonyl absorption in the infrared spectrum, thus tending to rule out a possible hemiketal structure. The *Z* stereochemistry shown is based on the formation of furyl-containing products upon carbonylation and the quantitative conversion of compound **6** to **7** upon refluxing in benzene (eq 12). Pure **7** can also be obtained easily by twice recrystallizing the crude mixture from benzene. The furan structure is supporting by ^{1}H NMR, elemental analysis, X-ray crystallography, and subsequent carbonylation results to be discussed later. While it is conceivable that compound **6** has stereochemistry opposite to that shown, the addition of mercuric chloride to the carbon–carbon triple bond must then be readily reversible as it is difficult to see how the furan products can come from any compound other than the *Z* isomer shown. It therefore appears that mercuric chloride undergoes syn addition to both compounds **3a** and **3b**, contrary to all previous reports of mercuric halide addition to acetylenes, including simple acetylenic alcohols[16-18] and ketones.[20]



(12)

6 7

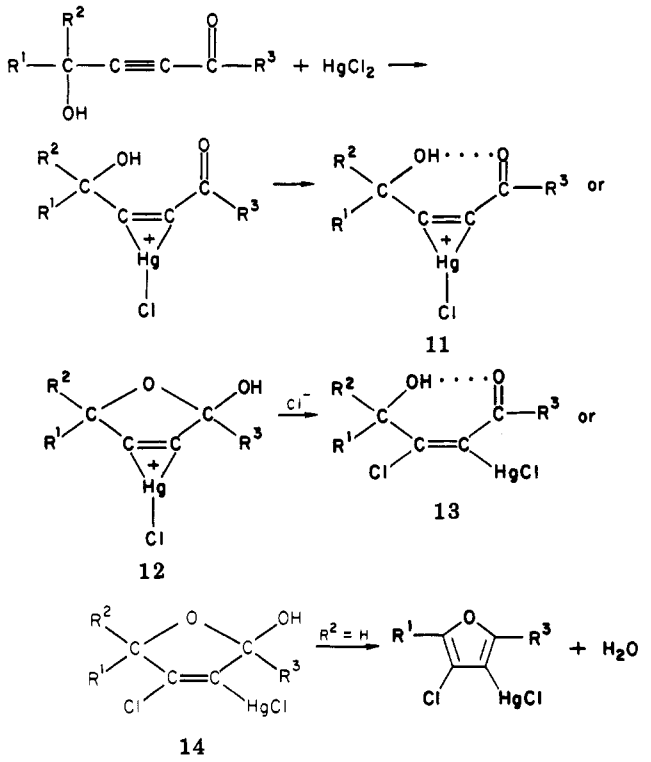
On the other hand, compound **3c** appears to afford the more normal anti adduct, **8**, upon mercuration. Only one pure compound is obtained, as judged by the ^{1}H and ^{13}C NMR spectra and elemental analysis. The presence of a strong carbonyl stretch in the infrared spectrum tends to rule out a hemiketal syn addition compound analogous to **5**. Unfortunately, we have been unable to grow crystals of this compound suitable for X-ray crystallographic analysis. Carbonylation of **8** proceeds to give a mixture of products, most important of which is the expected butenolide. Mercuration therefore appears to either proceed directly to the anti addition adduct **8** or forms the syn adduct, which isomerizes during carbonylation.

The mercuration of compound **3d** affords a high yield of a vinylmercurial, **9**, whose stereochemistry we have established by X-ray crystallographic analysis. Elemental analysis and ^{1}H and ^{13}C NMR spectra also indicate that only one isomer is formed. Upon attempted carbonylation of **9** only the starting material is recovered.

Finally, the mercuration of **3e**, a possible precursor for the synthesis of carolic acid,[52] has been examined. The only product to precipitate from solution is the furylmercurial **10** isolated in 17% unoptimized yield. The structure of **10** has been confirmed by elemental analysis as well as infrared and high-resolution ^{1}H NMR spectroscopy. This product apparently arises from mercuric chloride syn addition to the carbon–carbon triple bond followed by cyclic hemiketal formation and dehydration.

Mechanism of Mercuration. While the present evidence does not allow one to make any definition statements on the mechanism of these mercuration reactions, it is, we believe, worthwhile speculating on why the mercuration of 4-hydroxy-2-alkyn-1-ones apparently proceeds in a syn manner, at least with primary and secondary alcohols, but affords anti addition compounds with simple propargylic alcohols and compound **3c**. It should be pointed out that the stereochemistry of the mercuric chloride addition to 1-phenyl-1-butyn-3-one has not been established.[20]

Scheme I



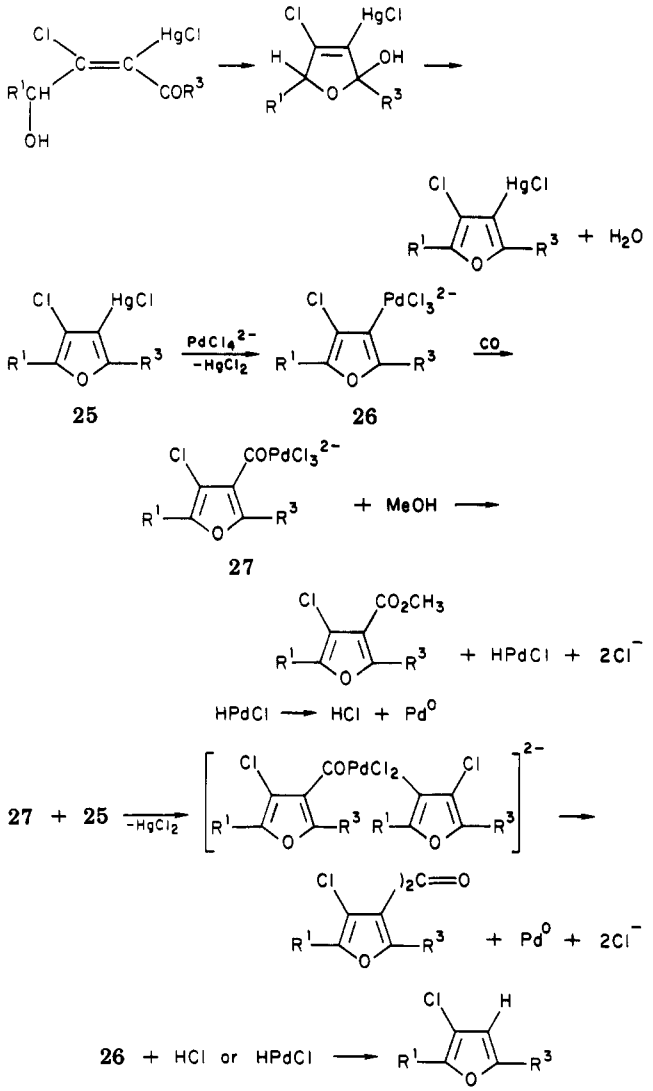
We assume that the mercuration of acetylenes parallels that of simple alkenes and that an initial π-complex or mercurinium ion like structure is initially produced (Scheme I). With 4-hydroxy-2-alkyn-1-ones, such as intermediate might be additionally stabilized by the presence of an intramolecular hydrogen bond between the alcohol and carbonyl groups (**11**) or by intramolecular hemiketal formation (**12**). Such cyclic structures would prevent backside attack of chloride anion on the carbon β to the carbonyl and allow only formation of the syn addition compounds by frontside attack on the mercury-stabilized cation, resulting is products such as **13** and **14** for which we have presented evidence in this paper. Furan formation is easily envisioned from such products by dehydration of the hemiketal **14**. Neither simple acetylenic alcohols nor ketones are capable of forming such hydrogen-bonded or cyclic structures. To examine the effect of hydrogen bonding we have examined the mercuration of the tetrahydropyranyl ethers **2c** and **2b** and the acetate corresponding to **2b**. Unfortunately, **2c** decomposed and **2b** gave only **7** after considerable reaction time. Presumably **2b** is first hydrolyzing to the corresponding alcohol **3b**, which only then undergoes mercuration. The acetate corresponding to **2b** gave no reaction with aqueous mercuric chloride. Unfortunately, we are therefore unable to assess the role of hydrogen bonding in these reactions except to say that the free OH group appears necessary for reaction. Otherwise, this mechanisms nicely explains the majority of our results. It does not, however, provide an answer as to why the tertiary alcohol **3c** or ester **3d** apparently afford anti addition compounds. One can only

Table II. Carbonylation of Organomercurials 6 and/or 7

organomercurial(s)	solvent	base added	products (ratio[a])	% yield[b]
6	MeOH	--	18:19a:20 (4.6:2.2:1)	11 (19a)
				4 (20)
		MgO	19a	12
	Et_2O	--	18:19b:20 (12.4:1:3.7)	
		$2Et_3N$	18:19b:20 (1:3.6:28)	
	CH_3CN	--	18:20 (1:1.7)	
		$2Et_3N$	20	(8)
6 + 7[c]	MeOH	--	18:19a:20 (7:1:1.2)	
		$2Et_3N$	19a	(9)
		MgO	19a	(10)
	CH_3CN	MgO	18:19c:20 (1.2:1:3.6)	(10) (20)
		$4Et_3N$	20	(3)
7	MeOH	$2Et_3N$	19a	(97)
	CH_3CN	$2Et_3N$	20	(93)

[a] The ratio indicates the relative peak areas as determined from GLC analysis. [b] Isolated yield (yield determined by GLC analysis). [c] Ratio of 6 to 7 is approximately 95:5.

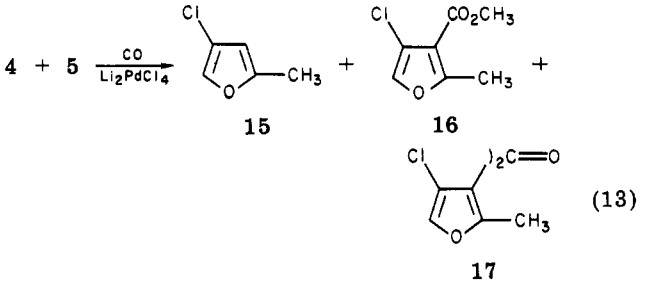
Scheme II



surmise that cyclic structures such as 11 and 12 might be less favorable with the more highly crowded tertiary alcohol of 3c or the ester carbonyl of 3d and do not form to any significant extent, therefore allowing chloride anion to attack the mercury cation from the backside.

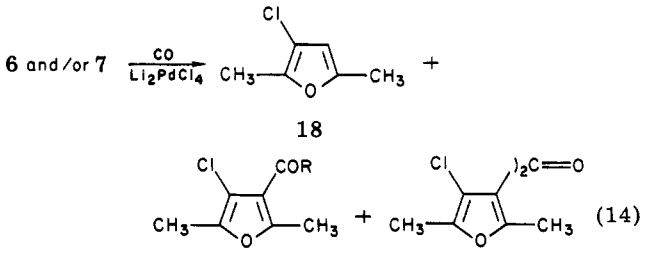
Carbonylation. Much of the information used to help establish the structure of the various organomercurials prepared in the previous section has been obtained by studying the palladium-promoted carbonylation of these compounds. This approach has previously proven valuable for the synthesis of β-chloro-$\Delta^{\alpha,\beta}$-butenolides from the anti adducts obtained from mercuric chloride addition to simple propargylic alcohols (eq 6).[17,18] It was, in fact, with the expectation that we would obtain butenolides that the present carbonylation studies were initiated. This work has resulted instead in a novel new route to furan-containing carbonyl compounds as well as providing the first evidence for the syn addition of mercuric chloride to acetylenes.

Since neither vinylmercurial 4 nor 5 can be isolated in pure form, a mixture of these two compounds of unknown ratio has been carbonylated using 1 equiv of Li_2PdCl_4, 1 atm of carbon monoxide, and either methanol or diethyl ether as the solvent (eq 13). Only furan-containing compounds 15, 16, and 17 have been observed, and the first two compounds have been identified by gas chromatography/mass spectral analysis only. In ether, compound 15 is the major product, but it proved too volatile to easily isolate. Compound 17 is also formed in 30% isolated yield in this reaction. In methanol, all three compounds, 15, 16, and 17, are formed in the approximate ratio 130:25:1, respectively, based on relative peak areas in the gas chromatograph.



(13)

Pure vinylmercurial 6, a 95:5 mixture of 6 and 7, and pure 7 have also been carbonylated (eq 14). Furan-containing products analogous to those obtained upon carbonylation of 4 + 5 have been obtained. The results are

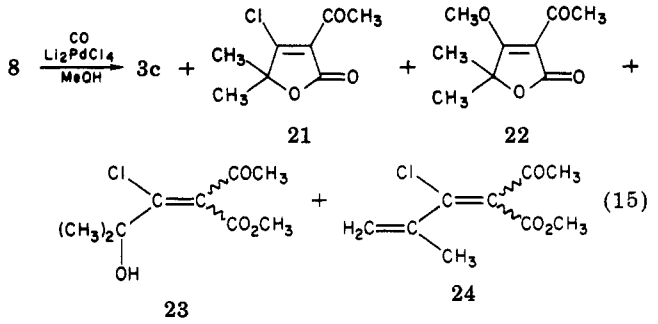


(14)

19a, R = OCH_3
19b, R = OC_2H_5
19c, R = Cl

summarized in Table II. Compounds **18**, **19b**, and **19c** have been characterized by gas chromatography/mass spectrometry only. Unfortunately, only low yields of products could be isolated from **6** or **6** + **7**. While the addition of a base greatly reduces the amount of **18** in these reactions, the isolated yields of **19** or **20** are not significantly improved. In diethyl ether, ethyl esters are actually observed, indicating that the ether is being cleaved in some fashion. Starting with pure **7**, one can obtain near quantitative yields of the methyl ester **19a** in methanol or the corresponding ketone **20** in acetonitrile.

The carbonylation of **8** leads to a variety of products (eq 15). Compound **3c** has been characterized by comparison



(15)

of its gas chromatographic retention time and mass spectrum with that of authentic **3c**. Compounds **21** and **22** have been isolated and fully characterized, while evidence for **23** and **24** rests solely on gas chromatography/mass spectral data. In the absence of a base, **3c**, **21**, **22**, and **23** are formed in the ratio 16:3:1:2 (relative peak areas obtained by GLC analysis). With 1 equiv of MgO added, all five compounds are observed by GLC analysis in the following relative amounts **23** > **3c** > **21** > **24** > **22**. However, only compounds **21** (12%) and **22** (4%) could be isolated and identified. With 1 equiv of triethylamine added, compounds **3c**, **21**, and **23** were observed in the ratio 10:1:1 (GLC peak areas). Compound **8** is the only organomercurial to afford both starting acetylene and butenolide products upon carbonylation. This suggests that **8** probably has stereochemistry opposite to that of **4** or **6**.

The carbonylation of compound **9** has been studied under a variety of reaction conditions. No carbonylation products were observed, and 50–60% of the starting vinylmercurial could be recovered.

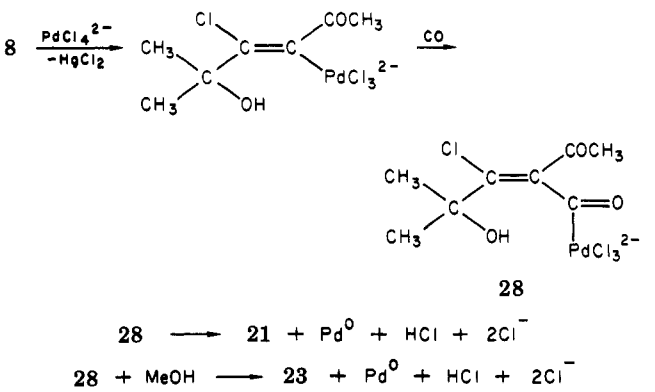
The carbonylation of furylmercurial **10** has not been studied.

The furan-containing carbonyl products are most likely formed by cyclic dehydration of the vinylmercurials to furylmercurials followed by carbonylation according to Scheme II. Compounds **21** and **23** presumably arise as shown in Scheme III.

Conclusions

The addition of mercuric chloride to acetylenes has been reported to give vinylmercuric chlorides where the chlorine and mercury groups are anti to each other. We have examined the mercuration of 4-hydroxy-2-alkyn-1-ones and observed that, at least with primary and secondary alcohols, mercuric chloride appears to add syn to the carbon–carbon triple bond. These vinylmercurials undergo facile cyclic dehydration to furylmercuric chlorides in the presence of dilute HCl or upon simple recrystallization. This provides a unique approach to 3-substituted furans since the mercury moiety can be readily converted into a variety of other substituents. For instance, carbonylation affords either the corresponding methyl ester or symmetrical ketone in near quantitative yields. With a tertiary

Scheme III



alcohol, it appears that mercuric chloride adds anti to the acetylene. Carbonylation affords the corresponding butenolide plus other products. The exact reason for the difference in products remains obscure.

Experimental Section

Equipment. The infrared spectra were recorded on a Beckman IR-4250 infrared spectrophotometer and the ^1H NMR spectra on a Varian Associates A-60 NMR or a Hitachi Perkin-Elmer R-20 B NMR spectrometer. High-resolution ^1H NMR spectra were recorded on a Bruker WM-300 NMR spectrometer. Carbon-13 NMR spectra were recorded on a JEOL FX-90Q NMR spectrometer. The mass spectra were obtained on an AEI MS-902 high-resolution mass spectrometer, while the GC/mass spectra were recorded on a Finnegan 4023 GC/MS data system. GLC analyses were performed on a Varian 3700 gas chromatograph with an attached Varian CDS-111 chromatography data system. Thin-layer chromatography was performed on Merck 60F-254 silica gel plates from MCB Manufacturing Chemists, Inc. Silica gel for column chromatography was purchased from Davison Chemical (60–200 mesh) and MCB Manufacturing Chemists, Inc. (230–400 mesh).

Reagents. All chemicals were used directly as obtained unless otherwise indicated. Propargyl alcohol was purchased from Aldrich and 3-hydroxy-1-butyne and 3-hydroxy-3-methyl-1-butyne from Farchan. Acetic anhydride, mercuric chloride, and sodium chloride were used directly as obtained from Fisher. Dihydropyran (Eastman Kodak) and γ-butyrolactone (Aldrich) were distilled before using. Methanol was distilled from magnesium methoxide; acetonitrile was distilled from phosphorus pentoxide; diethyl ether and tetrahydrofuran were distilled from calcium hydride; and triethylamine was distilled from barium oxide before using. Magnesium oxide and lithium chloride were purchased from J. T. Baker. Palladium chloride was generously supplied by Johnson Matthey, Inc., and Engelhard Industries. Carbon monoxide was purchased from Matheson Gas Products.

Preparation of Tetrahydropyranyl Ethers of Propargylic Alcohols. All preparations were carried out under conditions identical with those described by Parham.[66] The preparation of 3-(tetrahydropyranyloxy)-1-propyne (**1a**) is representative. To a mixture of 3-hydroxy-1-propyne (1.12 mol) and dihydropyran (1.12 mol) was added a few drops of concentrated hydrochloric acid, and the mixture was allowed to stand for 3 h with occasional shaking. Ether was then added and the solution was shaken vigorously with 10% aqueous sodium hydroxide to ensure removal of all traces of acid. The ethereal extract was dried (Na_2SO_4), concentrated, and distilled, giving 148.6 g (91%) of the tetrahydropyranyl ether **1a**: bp 40–43 °C (1 mmHg); ^1H NMR (CCl_4) δ 1.3–2.0 (br m, 6 H, CH_2), 2.35 (t, 1 H, J = 2.5 Hz, C≡CH), 3.2–4.0 (m, 2 H, $-CH_2O-$), 4.15 (d, 2 H, J = 2.5 Hz, $CH_2C{\equiv}C$), 4.76 (br s, 1 H, $-OCHO-$); IR (neat) 3300 (C≡CH), 2120 (C≡C), 1120 (C—O) cm^{-1}.

The following two tetrahydropyranyl ethers were prepared in identical fashion. 3-(Tetrahydropyranyloxy)-1-butyne (**1b**): yield 85%; bp 28–30 °C (0.2mmHg); ^1H NMR (CCl_4) δ 1.42 (d, 3 H,

(66) Parham, W. E.; Anderson, E. L. *J. Am. Chem. Soc.* **1948**, *70*, 4187.

J = 6.8 Hz, CH_3), 1.61 (m, 6 H, CH_2), 2.27 (d, 1 H, J = 2.3 Hz, C≡CH), 3.20–3.97 (m, 2 H, $-CH_2O-$), 4.42 (qd, 1 H, J = 6.8 Hz, J = 2.3 Hz, OCH), 4.64–4.96 (br m, 1 H, OCHO); IR (neat) 3284 (C≡CH), 2098 (C≡C) cm^{-1}. 3-Methyl-3-(tetrahydropyranyloxy)-1-butyne (**1c**): yield 89%; bp 45–48 °C (1.5mmHg); ^1H NMR (CCl_4) δ 1.20–2.0 (br m, 6 H, CH_2), 1.44 (s, 3 H, CH_3), 1.49 (s, 3 H, CH_3), 2.37 (s, 1 H, C≡CH), 3.15–4.10 (m, 2 H, $-CH_2O-$), 4.94–5.17 (br m, 1 H, –OCHO–); IR (neat) 3300 (C≡CH), 2104 (C≡C) cm^{-1}.

Preparation of 4-(Tetrahydropyranyloxy)-2-alkyn-1-ones 2a-e. All preparations were carried out according to the method of Duranti and Balsamini with only slight modifications.[62] The following preparation of 1-(tetrahydropyranyloxy)-4-oxo-2-pentyne (**2a**) is representative of the general procedure used for the synthesis of compounds **2a–c**. To a −78 °C solution of 56.0 g (0.4 mol) of **1a** in 400 mL of tetrahydrofuran (THF) was slowly added 160 mL of 2.5 M n-butyllithium (0.4 mol). The mixture was stirred at −78 °C for 1 h and at −20 °C for 20 min. Then the solution was cooled back to −78 °C and transferred via a double-ended needle into a solution of acetic anhydride (0.48 mol) in 300 mL of THF also kept at −78 °C. The reaction mixtures was allowed to slowly warm up to room temperature over a period of 3 h and stirred overnight at room temperature. Ether (500 mL) was added and the mixture was then washed with saturated ammonium chloride solution. The organic layer was separated and the aqueous layer was extracted 3 times with ether. The organic extracts were combined, dried ($MgSO_4$), concentrated, and distilled, giving 10.6 g (19%) of starting material (**1a**) and 39.3 g (54%) of compound **2a**: bp 89–92 °C (0.3mmHg) [lit.[62] bp 93 °C (1 mmHg)]; ^1H NMR (CCl_4) δ 1.10–1.90 (m, 6 H, CH_2), 2.27 (s, 3 H, $COCH_3$), 3.4–4.0 (m, 2 H, $-OCH_2-$), 4.32 (s, 2 H, $-OCH_2C≡C$), 4.72 (br s, 1 H, –OCHO–); IR (neat) 2200 (C≡C), 1683 (C=O) cm^{-1}.

Compounds **2b** and **2c** were prepared in identical fashion. Compound **2b**: yield 61% (9% recovery of starting material **1b**); bp 77–78 °C (0.16mmHg); ^1H NMR ($CDCl_3$) δ 1.40–2.00 (br m, 6 H, CH_2), 1.5 (d, 3 H, J = 6.9 Hz, CH_3), 2.34 (s, 3 H, $COCH_3$), 3.35–4.15 (m, 2 H, $-OCH_2-$), 4.71 (q, 1 H, J = 6.9 Hz, CHOTHP), 4.88 (br s, 1 H, –OCHO–); IR (neat) 2220 C≡C), 1686 (C=O) cm^{-1}; mass spectrum (M^+ − H), m/z calcd for $C_{11}H_{15}O_3$ 195.102 12, obsd 195.103 02. Compound **2c**: yield 54% (17% recovery of starting material **1c**); bp 69–71 °C (0.25mmHg); ^1H NMR (CCl_4) δ 1.20–2.00 (m, 6 H, CH_2), 1.47 (s, 3 H, CH_3), 1.52 (s, 3 H, CH_3), 2.26 (s, 3 H, $COCH_3$), 3.18–4.10 (m, 2 H, $-OCH_2-$), 4.25–5.14 (br m, 1 H, –OCHO–); IR (neat) 2204 (C≡C), 1680 (C=O) cm^{-1}; mass spectrum (M^+ − CH_3), m/z calcd for $C_{11}H_{15}O_3$ 195.102 12, obsd 195.102 83.

Compound **2d** was prepared as follows. To a solution of 14.0 g (0.1 mol) of **1a** in 400 mL THF was added 0.1 mol of n-butyllithium (hexane solution) at −78 °C. The mixture was allowed to slowly warm up to −20 °C and then cooled back down to −78 °C. The above solution was transferred via a double-ended needle into a solution of 18.9 g (0.2 mol) of methyl chloroformate in 300 mL THF at −78 °C. The reaction mixture was stirred at −78 °C for 10 min and at 0 °C for 100 min. Ether (500 mL) was added and the reaction mixture was washed with saturated ammonium chloride solution. The organic layer was separated and the aqueous layer extracted 3 times with ether. The organic extracts were combined, concentrated, and distilled, giving 16.0 g (81%) of the ester **2d**: bp 100–101 °C (0.30mmHg); ^1H NMR (CCl_4) δ 1.3–2.07 (br m, 6 H, CH_2), 3.24–4.20 (m, 2 H, $-OCH_2-$), 3.77 (s, 3 H, OCH_3), 4.34 (s, 2 H, $CH_2C≡C$), 4.76 (br s, 1 H, –OCHO–); IR (CCl_4) 2240 (C≡C), 1726 (C=O) cm^{-1}; mass spectrum (M^+ − H), m/z calcd for $C_{10}H_{13}O_4$ 197.081 38, obsd 197.081 00.

Compound **2e** was prepared as follows. To a solution of 3.08 g (20 mmol) of **1b** in 70 mL of THF was added 9 mL of n-butyllithium (2.27 M solution in hexane, 20.4 mmol) at −78 °C. The mixture was allowed to slowly warm up to −20 °C and then cooled back down to −78 °C. The above solution was added slowly to a solution of 2.07 g (24 mmol) γ-butyrolactone in 80 mL of THF at −78 °C. The reaction mixture was stirred at −78 °C for 2 h, 0 °C for 1 h, and room temperature for 30 min. Ether (200 mL) was added and the reaction mixture was washed with saturated ammonium chloride solution. The organic layer was separated and the aqueous layer was extracted with ether 3 times. The organic extracts were combined and concentrated, and the residue was flash chromatographed (silica gel column, eluting solvent 1:1 EtOAc:hexanes) to afford 2.60 g (54%) of compound **2e**: ^1H NMR ($CDCl_3$) δ 1.33–2.20 (m, 8 H, CH_2), 1.53 (d, 3 H, J = 7 Hz, CH_3), 2.46 (br s, 1 H, OH), 2.72 (t, 2 H, J = 7.2 Hz, $CH_2C=O$), 3.34–4.14 (m, 2 H, $-OCH_2-$), 3.66 (t, 2 H, J = 6.5Hz, CH_2OH), 4.70 (q, 1 H, J = 7 Hz, CH), 4.90 (br s, 1 H, –OCHO–); IR (neat) 3100–3650 (OH), 2224 (C≡C), 1665 (C=O) cm^{-1}; mass spectrum (M^+ − H_2O), m/z calcd for $C_{12}H_{18}O_3$ 222.125 59, obsd 222.126 03.

Preparation and Mercuration of Compounds 3a–e. The following preparation of compound **6** is representative. To a solution of 1.96 g (10 mmol) of **2b** in 50 mL of 95% EtOH was added 0.252 g (1 mmol) of pyridinium p-toluenesulfonate (PPTS). The mixture was stirred at 80 °C (bath temperature) for 5 h. Analysis by TLC at this stage showed no starting THP ether. The mixture was cooled to room temperature, and the solvent was removed under reduced pressure. The residue was passed through a short column of silica gel (10–15 g, 1:1 EtOAc:hexanes) to remove PPTS. Without further purification compound **3b** was dissolved in 2 mL of MeOH and then added to 50 mL of a saturated aqueous solution of mercuric chloride and sodium chloride at room temperature. The reaction mixture was stored in the refrigerator for 10–12 h. The white solid that precipitated from solution was collected by vaccum filtration and washed with a small amount of cold water. The white solid was dried under vacuum for 24 h to afford 3.45 g (90%) of compound **6** containing a small amount of compound **7**. Fractional recrystallization of the crude product from benzene and collection of the first crop of crystals afforded pure compound **6**: recrystallized yield 27%; mp 119–120.5 °C; ^1H NMR (acetone-d_6) δ 1.50 (d, 3 H, J = 6.7 Hz, CH_3), 2.38 (s, 3 H, $COCH_3$), 4.68 (dq, 1 H, J = 6.7 Hz, J = 3.2 Hz, CH), 6.07 (br d, 1 H, J = 3.2 Hz, OH); IR ($HCCl_3$) 3590 (free OH), 3100–3520 (OH), 1674 (C=O), 1606 (C=C) cm^{-1}. Anal. Calcd for $C_6H_8Cl_2HgO_2$: C, 18.79; H, 2.10; Hg, 52.29; Cl, 18.48. Found: C, 18.75; H, 2.12; Hg, 52.28; Cl, 18.50.

The mother liquor was concentrated and recrystallized from benzene again to afford compound **7**: yield 40%; mp 185–185.5 °C; ^1H NMR (acetone-d_6) δ 2.22 (s, 3 H, CH_3), 2.36 (s, 3 H, CH_3); IR (KBr) 1590, 1560, 1520 (furan) cm^{-1}. Anal. Calcd for $C_6H_6HgCl_2O$: C, 19.71; H, 1.65; Hg, 54.86; Cl, 19.39. Found: C, 19.90; H, 1.61; Hg, 54.64; Cl, 19.53.

The following mercurials were prepared by the procedure described above and characterized. Compound **4** contains a small amount of compound **5**: yield 75% (recrystallized yield 30%); mp 154–155 °C; ^1H NMR for **4** (acetone-d_6) δ 2.43 (s, 3 H, CH_3), 4.52 (d, 2 H, J = 5.5 Hz, CH_2), 6.20 (t, 1 H, J = 5.5 Hz, OH); IR (KBr) 3200–3600 (OH), 1659 (C=O), 1633 (C=C) cm^{-1}. Compound **8**: yield 100% (recrystallized yield 72%); mp 139–140 °C dec; ^1H NMR (acetone-d_6) δ 1.56 (s, 6 H, CH_3), 2.32 (s, 3 H, $COCH_3$), 5.80 (s, 1 H, OH); IR (KBr) 3200–3600 (OH), 1670 (C=O), 1610 (C=C) cm^{-1}; ^{13}C NMR (acetone-d_6) δ 28.37 (2 CH_3), 29.47 (CH_3CO), 73.76 (COH), 144.71 and 148.02 (C=C), 203.5 (C=O). Anal. Calcd for $C_7H_{10}HgCl_2O_2$: C, 21.14; H, 2.53; Hg, 50.44; Cl, 17.83. Found: C, 21.48; H, 2.61; Hg, 49.97; Cl, 17.55. Compound **9**: yield 100% (recrystallized yield 72%); mp 155.5–156 °C; ^1H NMR (acetone-d_6) δ 3.71 (s, 3 H, OCH_3), 4.39 (s, 2 H, CH_2), 6.00 (br s, 1 H, OH); IR ($HCCl_3$) 3200–3600 (OH), 1722 (C=O), 1610 (C=C) cm^{-1}; ^{13}C NMR (acetone-d_6) δ 52.2 (OCH_3), 64.4 (CH_2O), 137.5 and 144.6 (C=C), 169.0 (C=O). Anal. Calcd for $C_5H_6HgCl_2O_3$: C, 15.57; H, 1.57; Hg, 52.02; Cl, 18.39. Found: C, 15.65; H, 1.60; Hg, 51.71; Cl, 18.05. Compound **10**: yield 17% (recrystallized yield 13%); mp 130.5–131 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 1.57 (t, 1 H, J = 4.9 Hz, OH), 1.80–1.88 (t t, 2 H, J = 6.8 Hz, J = 5.85 Hz, CH_2), 2.24 (s, 3 H, CH_3), 2.73 (t, 2 H, J = 6.8 Hz, CH_2), 3.69 (d t, 2 H, J = 5.85 Hz, J = 4.89 Hz, CH_2O); IR (KBr) 3050–3600 (OH), 1597, 1560 and 1513 (furan) cm^{-1}. Anal. Calcd for $C_8H_{10}Cl_2HgO_2$: C, 23.46; H, 2.46; Hg, 48.96; Cl, 17.31. Found: C, 23.62; H, 2.50; Hg, 48.83; Cl, 17.14.

Carbonylation. All carbonylation reactions were carried out according to the following representative procedure. Two millimoles of anhydrous lithium chloride (0.085g), 1 mmol of palladium chloride (0.1774g), 1 mmol of magnesium oxide (or 2 mmol of triethylamine if base was used), and 10 mL of dry solvent were placed in a round bottom flask with a septum inlet. While the system was being flushed with carbon monoxide at −78 °C, 1 mmol of the appropriate organomercurial was added. A balloon filled with CO was connected to the top of the flask, and the reaction

mixture was allowed to slowly warm up to room temperature and then stirred at room temperature for 24–48 h. One milliliter of saturated ammonium chloride solution, 30 mL of ether, and a small amount of activated carbon were added, and stirring was continued for an additional 30 min. The reaction mixture was filtered through Celite and washed with saturated ammonium chloride. The organic layer was dried (Na_2SO_4) and concentrated, and the reaction products were isolated by either liquid column chromatography or flash chromatography.

Carbonylation of compound **4** in diethyl ether (no base added) gave compounds **15** and **17** in a 3:1 ratio. Compound **15**: GC/MS, m/z (relative intensity, assignment) 118 (31.90, $M^+ + 2$), 116 (100, M^+), 87 (38.81, $M^+ - HCO$), 81 (12.57, $M^+ - Cl$), 53 (91.22, $M^+ - CO - Cl$). Compound **17**: yield 30%; mp 54–56 °C; ^1H NMR ($CDCl_3$) δ 2.48 (s, 6 H, CH_3), 7.48 (s, 2 H, CH); IR ($HCCl_3$) 3180 (C=CH), 1650 (C=O), 1590 and 1540 (furan) cm^{-1}; mass spectrum, m/z calcd for $C_{11}H_8Cl_2O_3$ 257.985 05, obsd 257.984 50. Anal. Calcd for $C_{11}H_8Cl_2O_3$: C, 50.99; H, 3.11. Found: C, 50.59; H, 3.44. The analogous reaction in methanol (no base added) gave products **15**, **16**, and **17** in the ratio 130:1:25. Compound **16**: GC/MS, m/z (relative intensity, assignment) 176 (13.24, $M^+ + 2$), 174 (41.85, M^+), 159 (16.72, $M^+ - CH_3$), 143 (100, $M^+ - OCH_3$), 114 (14.82, $M^+ - HCO_2CH_3$), 51 (70.88, $M^+ - 115$). The analogous reaction in methanol with 2 equiv of triethylamine added gave no products at all.

Carbonylation of compound **6** in methanol (no base added) gave products **18**, **19a**, and **20** in the ratio 4.6:2.2:1. Compound **18**: GC/MS, m/z (relative intensity, assignment) 132 (30.88, $M^+ + 2$), 131 (32.87, $M^+ + 1$), 130 (100, M^+), 129 (85.97, $M^+ - 1$), 115 (28.79, $M^+ - CH_3$), 95 (24.81, $M^+ - Cl$), 87 (33.82, $M^+ - CH_3 - CO$). Compound **19a**: yield 11%; ^1H NMR ($CDCl_3$) δ 2.25 (s, 3 H, CH_3), 2.52 (s, 3 H, CH_3), 3.86 (s, 3 H, OCH_3); IR ($HCCl_3$) 1719 (C=O), 1625 and 1572 (furan) cm^{-1}; mass spectrum, m/z calcd for $C_8H_9ClO_3$ 188.024 02, obsd 188.024 76. Compound **20**: yield 4%; mp 109–110 °C; ^1H NMR ($CDCl_3$) δ 2.28 (s, 3 H, CH_3), 2.40 (s, 3 H, CH_3); IR ($HCCl_3$), 1640 (C=O), 1570 (furan)cm^{-1}; mass spectrum, m/z calcd for $C_{13}H_{12}Cl_2O_3$ 286.016 35, obsd 286.016 23. The analogous reaction in methanol (1 equiv of MgO added) gave compound **19a** (12%) as the only product. Carbonylation in diethyl ether (no base added) gave compounds **18**, **20**, and **19b** in ratio 12.4:3.7:1. Compound **19b**: GC/MS, m/z (relative intensity, assignment) 204 (14.61, $M^+ + 2$), 202 (46.85, M^+), 173 (100, $M^+ - C_2H_5$), 157 (72.58, $M^+ - OC_2H_5$), 128 (24.59, $M^+ - HCO_2C_2H_5$). The same reaction in diethyl ether with 2 equiv of triethylamine added gave **18**, **20**, and **19b** in the ratio 1:28:3.6. Reaction in acetonitrile (no base added) gave the two products, **18** and **20**, in the ratio 1:1.7. Carbonylation in acetonitrile (2 equiv of triethylamine added) afforded only one product, **20**, in 8% GLC yield.

Carbonylation of compound **7** in methanol (2 equiv of triethylamine added) gave only one product, **19a**, in 97% yield. Reaction in acetonitrile (2 equiv of triethylamine added) yielded compound **20** in 93% yield.

Carbonylation of a mixture containing compounds **6** and **7** in methanol (no base added) afforded three products, **18**, **19a**, and **20**, in the ratio 7:1:1.2. The same reaction with 2 equiv of triethylamine added afforded only one product, **19a**, in a 9% yield. One equivalent of MgO yielded 10% of compound **19a** as the only product. Carbonylation in acetonitrile (1 equiv of MgO added) gave three products, **18**, **20**, and **19c**, in the ratio 1.2:3.6:1 Compound **20** was isolated in 10% yield. Compound **19c**: GC/MS (relative intensity, assignment) 194 (6.07, $M^+ + 2$), 192 (10.34, M^+), 159 (31.79, $M^+ + 2 - Cl$), 157 (100, $M^+ - Cl$), 129 (3.42, $M^+ - COCl$). Reaction in acetonitrile (4 equiv of triethylamine added) gave compound **20** as the only product in 3% yield. The results of the carbonylation of **6** and/or **7** are summarized in Table II.

Carbonylation of compound **8** in methanol (1 equiv of MgO added) gave products **3c** and **21–24**. Compound **3c**: GC/MS, m/z (relative intensity, assignment) 126 (100, M^+), 111 (3.05, $M^+ - CH_3$), 68 (88.86, $M^+ - C_3H_6O$). Compound **21**: yield 12%; ^1H NMR (CCl_4) δ 1.57 (s, 6 H, CH_3), 2.47 (s, 3 H, $COCH_3$); IR (CCl_4) 1777 (lactone), 1703 (ketone), 1607 (C=C) cm^{-1}; mass spectrum, m/z calcd for $C_7H_9ClO_3$ 188.024 03, obsd 188.024 37. Compound **22**: yield 4%; ^1H NMR (CCl_4) δ 1.45 (s, 6 H, CH_3), 2.47 (s, 3 H, $COCH_3$), 4.12 (s, 3 H, OCH_3); IR (CCl_4) 1760 (lactone), 1684 (ketone), 1604 (C=C) cm^{-1}; GC/MS, m/z (relative intensity, assignment) 184 (100, M^+), 169 (82.19, $M^+ - CH_3$), 141 (24.06, $M^+ - CH_3CO$). Compound **24**: GC/MS, m/z (relative intensity, assignment) 204 (31.51, $M^+ + 2$), 202 (100, M^+), 187 (66.13, $M^+ - CH_3$), 170 (52.16, $M^+ - MeOH$), 167 (18.32, $M^+ - Cl$), 143 (40.28, $M^+ - CO_2CH_3$). Compound **23**: GC/MS, m/z (relative intensity, assignment) 222 (1.01, $M^+ + 2$), 220 (3.30, M^+), 219 (35.93, $M^+ - 1$), 203 (100, $M^+ - OH$), 187 (8.66, $M^+ - H_2O - CH_3$), 171 (7.38, $M^+ - H_2O - OCH_3$), 143 (4.48, $M^+ - H_2O - CO_2CH_3$). Carbonylation in methanol (no base added) gave products **3c**, **21**, **22**, and **23** in the ratio 16:3:1:2, while addition of 1 equiv of triethylamine gave **3c**, **21**, and **23** in the ratio 10:1:1. Reaction in acetonitrile (2 equiv of triethylamine added) gave no organic product at all.

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