Intramolecular Benzannulation Reactions of Chromium Siloxycarbene Complexes: Regiochemical Control and the "Xenochemical Effect" of Alkyne Additives

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Received June 28, 1993[⊗]

Abstract: Acetylenic alcohols are attached to chromium oxycarbene fragments via dialkylsilicon linkages in convenient fashion to provide siloxycarbene complexes which undergo intramolecular benzannulation upon heating. Yields of alkynol-derived quinone products after oxidative workup increase markedly when the reactions are conducted in the presence of the "external" alkynes diphenylacetylene, 3-hexyne, or 1-hexyne. The action of alkyne additives, which participate in competitive intermolecular benzannulation to only a minor extent, is inhibited by donor solvent or carbon monoxide. Kinetics measurements demonstrate that the benzannulation reactions are initiated by dissociative CO loss. The alkyne additives are believed to act by coordination to vinylcarbene intermediates produced by intramolecular alkyne insertion, consistent with previous suggestions. A carbon-tethered analogue was found to be unresponsive to the addition of external alkyne. Evidence for the reversible nature of alkyne insertion and the bimolecular decomposition of siloxycarbene complexes is discussed. The methodology provides products with complete regiospecificity regardless of the size of the tethered alkyne substituents, including those not directly accessible by intermolecular reactions of terminal alkynes.

The benzannulation reaction,[1] which incorporates an α,β-unsaturated carbenoxy moiety of a Fischer carbene complex, an alkyne, and a CO ligand, is among the most widely used of the transformations of Fischer carbene complexes for the purposes of organic synthesis.[2] It also comprises a fascinating case for mechanistic consideration, with three fundamental steps having been proposed and in some cases substantiated by studies of reaction products and characterization of intermediates:[2,3] insertion of the alkyne into the M=C double bond to give vinylcarbenes,[4] intramolecular CO insertion to give coordinated vinylketenes,[5] and vinylketene ring closure to construct the six-membered phenolic skeleton.[6] Such a mechanism has many possible branch points for side reactions, and indeed the reactions of alkynes with Fischer carbene compounds have given rise to more than a dozen distinct types of products depending on reaction conditions and substituents.[2] It is a measure of the richness of this chemistry that, nearly 20 years after the discovery of the first example,[1] the development of new reaction patterns and means for their control remains the subject of active investigation.[7]

Intermolecular benzannulation reactions of chromium carbene complexes proceed with excellent regioselectively when there is a relatively large difference in the size of the two alkyne substituents, as with terminal alkynes, but with poor selectivity

[⊗] Abstract published in *Advance ACS Abstracts*, October 15, 1994.

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(6) For simplicity, the alternative mechanistic proposal of Casey,[2f] which features annulation of vinylcarbene intermediates followed by CO insertion and reductive elimination, is not discussed. While circumstantial evidence disfavors this mechanism, the fundamental aspects of the present discussion may be applied to it as well.

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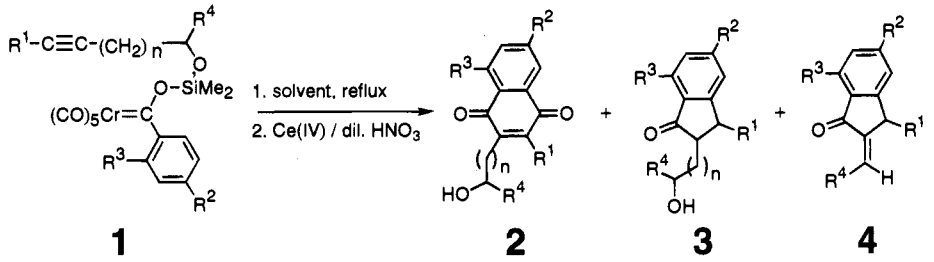
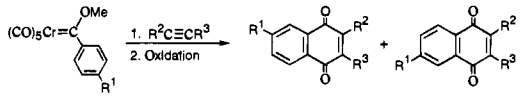
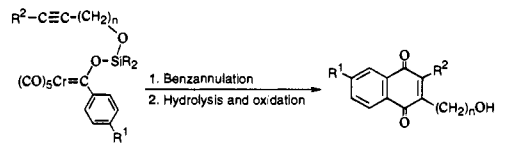


Figure 1. Intramolecular benzannulation reactions of siloxycarbene complexes.

when the alkyne substituents are of comparable size (eq 1).[2a,d,g,8] Here we report the development of intramolecular benzannulation reactions of chromium carbene complexes containing an alkyne unit tethered to the carbene heteroatom through a hydrolyzable silicon center. In this way, the regiochemistry of alkyne addition is controlled regardless of the relative sizes of alkyne substituents (eq 2),as has been previously accomplished



(1)



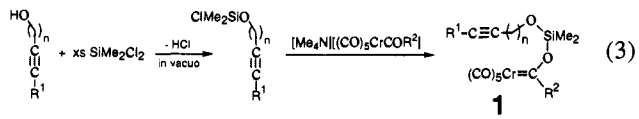
(2)

with carbon chain tethers;[9] the Si−O linkages employed here are more easily assembled and undone. Such regiochemical control has beneficial consequences for the use of benzannulation in the synthesis of natural products, since the reaction has thus far been applied largely[10] to targets incorporating terminal alkynes.[2a] Thus, the present method extends the intramolecular benzannulation strategy to convenient acetylenic alcohol substrates, providing products with a hydroxyl group that may be used for further elaboration, as illustrated by the efficient formal synthesis of (*dl*)-deoxyfrenolicin also outlined below.

We find that tethered acetylenic siloxycarbene complexes derived from both terminal and internal alkynols afford modest yields of naphthoquinones and small amounts of indanones. However, the addition of an excess of nontethered ("external") alkyne boosts the yields of naphthoquinones to a remarkable degree, equalling or surpassing the efficiency of carbon-linked systems previously employed for purposes of regiochemical control.[9] We have observed a similar effect in the benzannulation reactions of manganese siloxycarbene systems,[11] but not for a carbon-tethered alkoxycarbene complex (*vide infra*). The steric and electronic nature of carbene complex substituents have been found to modulate these alkyne effects in a manner that supports the intermediacy of vinylcarbene species. Kinetics measurements are discussed that substantiate the dissociative nature of rate-limiting CO loss from the starting siloxycarbene compounds. Thus, the effects of external alkyne addition provide an additional probe of the nature of kinetically invisible reaction intermediates. Evidence is presented concerning siloxycarbene complex decomposition suggesting that intramolecular alkyne insertion is rapidly reversible.

Results

Siloxycarbene Complex Preparation. Siloxycarbene complexes **1** were assembled in quantitative yield from acetylenic alcohols, $SiMe_2Cl_2$, and the appropriate pentacarbonylchromium acylate precursor as shown in eq 3. Addition of acetylenic



(3)

alcohol to an excess (5−10 equiv) of $SiMe_2Cl_2$, followed by removal of HCl and excess $SiMe_2Cl_2$ *in vacuo*,[12] provided alkynoxydimethylsilyl chlorides, which may be isolated or used *in situ*. The siloxycarbene compounds can be stored for periods of 1−2 weeks at −30 °C in the absence of air, are stable in deoxygenated solution for several hours at ambient temperature, and are used without additional purification.

Intramolecular Benzannulation in the Absence of External Alkyne. Siloxycarbene complexes **1a−q** underwent benzannulation upon heating in various solvents under inert atmosphere with the results summarized in Figure 1 and Table 1. The three major products were substituted naphthoquinones **2**, substituted indanones **3**, and α-methyleneindanones **4**, the latter produced for propargylic substrates ($n = 0$) from **3** in acidic oxidative workup. Prolonged exposure of reaction mixtures to the Ce^{IV}/HNO_3 workup conditions was found to lead to minor amounts of aldehydes and nitrates by reaction of the pendant alcohol group of **2** and **3** (see Experimental Section).

The intramolecular benzannulation reaction in the absence of alkyne additives is insensitive to concentration of the Cr complex. For example, the yields of quinone **2n** and indanone **3n** from siloxycarbene compound **1n** are unchanged in benzene upon dilution from 0.04 to 0.006 M (Table 1, entries 25 and 26). Table 1 shows that variations in solvent and tether chain length also produce little change in product yields.

Complexes bearing a long-chain substituent at the alkyne terminus give significantly higher yields than the other compounds shown. Thus, **1g**, **1h**, and **1i** ($R^1 = n\text{-}C_7H_{15}$) afford 48%, 36%, and 55% yields of quinone, respectively, compared to 33%, 21%, and 38% yields for the analogous complexes **1c**, **1d**, and **1e** ($R^1 = CH_3$). An additional example of this

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(10) An exception is the regioselective incorporation of disubstituted alkynes bearing primary alkyl or ether *vs* secondary groups. For examples, see: (a) Boger, D. L.; Jacobson, I. C. *J. Org. Chem.* **1991**, *56*, 2115−2122. (b) Boger, D. L.; Jacobson, I. C. *Tetrahedron Lett.* **1989**, *30*, 2037−2040. (c) Boger, D. L.; Jacobson, I. C. *J. Org. Chem.* **1990**, *55*, 1919−1928. (d) Yamashita, A.; Toy, A.; Scahill, T. A. *J. Org. Chem.* **1989**, *54*, 3625−3634. (e) Yamashita, A. *J. Am. Chem. Soc.* **1985**, *107*, 5823−5824.

(11) Balzer, B. L.; Cazanoue, M.; Finn, M. G. *J. Am. Chem. Soc.* **1992**, *114*, 8735−8736.

(12) Propargyl alcohol is an exception, which must be slowly added to a large excess (30 equiv) of $SiMe_2Cl_2$ at 0 °C to avoid disubstitution.

Table 1. Isolated Yields for Intramolecular Benzannulation Reactions in the Absence of Additives

entry		*n*	R^1	R^2	R^3	R^4	solvent[a]	**2**	**3**	**4**
1	**1a**	0	H	Me	H	H	THF	14		
2	**1b**	0	Me	H	H	H	THF	24[b]		
3	**1b**						hexane	34		
4	**1c**	0	Me	Me	H	H	THF	17	8	10
5	**1c**						benzene	19	2	16
6	**1c**						hexane	33		
7	**1c**						hexane[c]	28		
8	**1c**						hexane[d]	26	2	
9	**1d**	0	Me	OMe	H	H	hexane	21	trace	
10	**1e**	0	Me	H	OMe	H	hexane	38		
11	**1f**	0	Ph	Me	H	H	THF	25[b,e]		
12	**1f**						hexane	19[b,f]		
13	**1g**	0	n-C_7H_{15}	Me	H	H	hexane	48		
14	**1h**	0	n-C_7H_{15}	OMe	H	H	hexane	36[g]		
15	**1i**	0	n-C_7H_{15}	H	OMe	H	hexane	55[h]		
16	**1j**	1	H	Me	H	H	THF	23		
17	**1j**						benzene	24		
18	**1j**						hexane	26		
19	**1j**						hexane[c]	22		
20	**1k**	1	H	OMe	H	H	CH_2Cl_2	26[b]		
21	**1l**	1	H	Me	H	Me	THF	15		
22	**1m**	1	Me	H	H	H	THF	27	6	
23	**1m**						benzene[i]	25	3	
24	**1n**	1	Me	Me	H	H	THF	30	4	
25	**1n**						benzene[j]	27	5	
26	**1n**						benzene[k]	25	5	
27	**1n**						toluene	25[b]		
28	**1n**						hexane	27		
29	**1o**	1	Me	OMe	H	H	THF	20	6	
30	**1o**	1	Me	OMe	H	H	hexane	31		
31	**1p**	2	H	Me	H	H	THF	15		
32	**1q**	2	H	OMe	H	H	THF	30[b]		

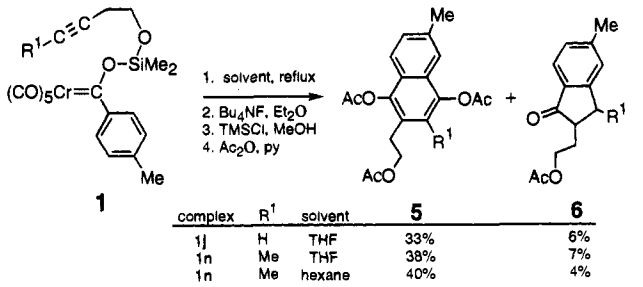
[a] Unless otherwise noted [Cr] ranges from 0.01 to 0.03 M. [b] Reaction screened only for **2**. [c] 2,6-Di-*tert*-butylpyridine and powdered 4Å molecular sieves added. [d] 1.5 equiv (0.015 M) acetic anhydride added. [e] Recovered 40% 3-phenyl-2-propyn-1-ol. [f] Yield of 3-phenyl-2-propyn-1-ol was not determined. [g] Recovered 50% 2-decyn-1-ol. [h] Recovered 25% 2-decyn-1-ol. [i] Workup consisted of treatment with Bu_4NF, protonation with dilute HCl, and oxidation with aqueous Ce(IV). [j] [Cr] = 0.04 M. [k] [Cr] = 0.006 M.

phenomenon is presented below (complex **20**, R^1 = allyl). The presence of phenyl substituent (complex **1f**) induces no such effect.

Low yields of annulated compounds are typically accompanied by benzil and benzoin-type decomposition products derived from two carbene fragments, as well as small amounts (<5%) of arylcarboxylic acids. For example, along with quinone in 22% yield, complex **1j** provides 4,4'-dimethylbenzil[13] (ArCOCOAr) in 32% yield (thus accounting for a total of 86% of the starting carbene complex) after oxidative workup. The addition of powdered 4 Å molecular sieves and 2,6-di-*tert*-butylpyridine to **1c** and **1l** in hexane resulted in no improvement in quinone yield (Table 1, entry 6 vs 7 and entry 18 vs 19, respectively), suggesting that trace water or acid is not responsible for decomposition. Acetic anhydride has been found to provide improved yields and greater reaction rates in certain intermolecular benzannulation reactions,[10] but it failed to alter the intramolecular reaction of complex **1c** (Table 1, entry 8). The use of larger alkyl groups on silicon made the resulting siloxycarbene compounds less active in both the absence and presence of external alkyne additives (*vide infra*): when the $SiMe_2$ linkage in **1c** was replaced by a $SiEt_2$ group, **2c** was obtained in much reduced yield, and a $Si(iPr)_2$ linkage rendered the carbene complex completely unreactive in refluxing hexane.

(13) Identified by ^1H NMR, ^{13}C NMR, and IR spectra matching the authentic compound purchased from Aldrich Chemical Co., as well as co-injection on capillary gas chromatography.

Scheme 1



The oxidative nature of the standard workup (ca. 10 equiv of Ce^{IV} in 0.1 M HNO_3) was shown to contribute slightly to the low yields. Crude reaction mixtures of **1j** and **1n** were subjected to a nonoxidative procedure involving treatment with fluoride ion followed by protonation and acylation. The yield of quinone-derived products **5** was found to increase from 23%, 30%, and 27% respectively to 33%, 38%, and 40% (Scheme 1).

Intramolecular Benzannulation in the Presence of External Alkyne. Wulff and co-workers have demonstrated that the distribution of products obtained from benzannulation reactions of chromium methoxycarbene complexes is dependent upon the concentration of alkyne substrate, coining the phrase "allochemical effect" to describe the action of an additional equivalent of alkyne as a ligand to modulate the reactivity of

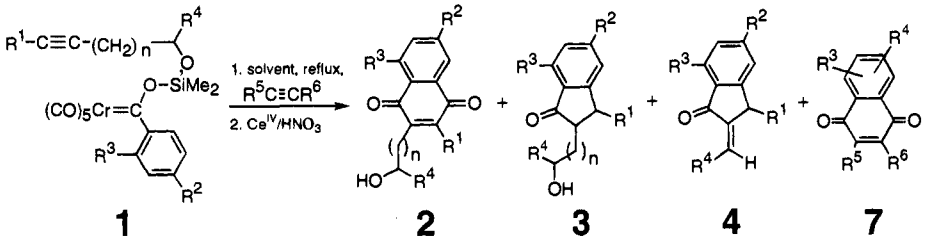


Figure 2. Intramolecular benzannulation reactions in the presence of alkyne additives.

Table 2. Isolated Yields for Intramolecular Benzannulation Reactions in the Presence of Additives

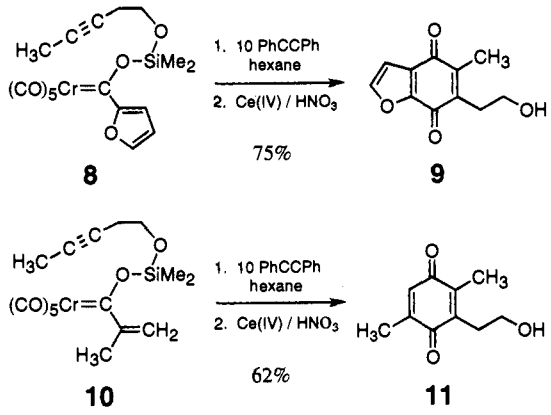
entry		n	R^1	R^2	R^3	R^4	solvent[a]	additive	additive	**2**	**3**	**4**	**7**
1	**1a**	0	H	Me	H	H	hexane	PhCCPh	10	40			
2	**1c**	0	Me	Me	H	H	THF	PhCCPh	10	26[e]		*b*	
3	**1c**						hexane	PhCCPh	2	50	6	*b*	
4	**1c**						hexane	PhCCPh	5	70	8	*b*	
5	**1c**						hexane[c]	PhCCPh	5	61	4	*b*	
6	**1c**						hexane	PhCCPh	10	83	3	*b*	
7	**1c**						hexane[c]	PhCCPh	10	85	3	*b*	
8	**1c**						hexane	PhCCPh	10[d]	45	6	*b*	
9	**1c**						hexane	1-hexyne	10	31	4		24
10	**1c**						hexane	3-hexyne	2	39	6		22
11	**1c**						hexane	3-hexyne	5	48	4	2	21
12	**1c**						hexane	3-hexyne	10	51	11	4	19
13	**1d**	0	Me	OMe	H	H	hexane	PhCCPh	10	39	trace		
14	**1d**						hexane	3-hexyne	10	29	trace		14
15	**1e**	0	Me	H	OMe	H	hexane	PhCCPh	10	62[e]			
16	**1f**	0	Ph	Me	H	H	hexane	PhCCPh	10	43[f]			
17	**1g**	0	n-C_7H_{15}	Me	H	H	hexane	PhCCPh	10	51[g]			
18	**1g**						hexane	3-hexyne	10	56[h]			
19	**1i**	0	n-C_7H_{15}	H	OMe	H	hexane	PhCCPh	10	49[i]			
20	**1r**	0	Me	Me	H	Et	hexane	3-hexyne	10	53		17	9
21	**1s**	0	Me	H	OMe	Et	hexane	PhCCPh	10	73[j]		4	
22	**1j**	1	H	Me	H	H	benzene	PhCCPh	2	22			
23	**1j**						hexane	PhCCPh	10	60			
24	**1j**						hexane	3-hexyne	10	41			14
25	**1t**	1	H	H	OMe	H	hexane	PhCCPh	10	41			
26	**1l**	1	H	Me	H	Me	hexane	PhCCPh	10	48			
27	**1n**	1	Me	Me	H	H	THF	PhCCPh	5	29	6		
28	**1n**						benzene	PhCCPh	10	55[e]			
29	**1n**						hexane	PhCCPh	10	65	5		
30	**1n**						hexane	1-hexyne	10	54			15
31	**1n**						hexane	3-hexyne	5	61	10		6
32	**1n**						hexane	3-hexyne	10	75			9
33	**1o**	1	Me	OMe	H	H	hexane	PhCCPh	10	55			
34	**1o**						hexane	3-hexyne	10	40	4		7
35	**1u**	1	Me	H	OMe	H	hexane	PhCCPh	10	59[e]			
36	**1p**	2	H	Me	H	H	hexane	PhCCPh	10	44			
37	**1p**						hexane	3-hexyne	10	25			12
38	**1v**	2	Me	Me	H	H	hexane	PhCCPh	10	50			
39	**1v**	2					hexane	3-hexyne	10	25			14
40	**1w**	2	Me	OMe	H	H	hexane	PhCCPh	10	37			
41	**1x**	2	Me	H	OMe	H	hexane	PhCCPh	10	65			

[a] Unless otherwise noted [Cr] = 0.01 M. [b] Not determined, since **4** and PhCCPh were not separated by thin-layer or column chromatography. [c] [Cr] = 0.001 M. [d] Reaction performed under 1 atm of CO. [e] Reaction screened only for **2**. [f] Recovered 37% 3-phenyl-2-propyn-1-ol. [g] Recovered 25% 2-decyn-1-ol. [h] Recovered 31% 2-decyn-1-ol. [i] Recovered 40% 2-decyn-1-ol. [j] Isolated 4% of the ketone.

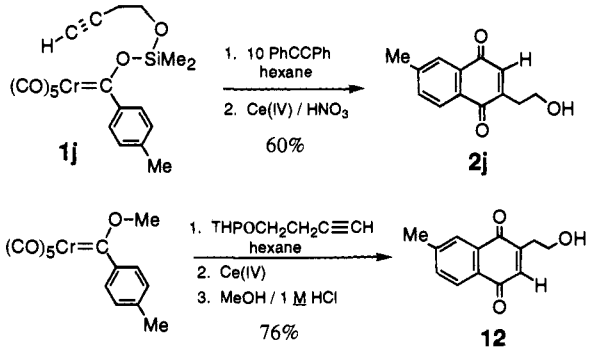
one or more reaction intermediates.[3b] This led us to discover striking improvements in yields of intramolecular benzannulation reactions of manganese siloxycarbene complexes upon the addition of an excess of diphenylacetylene.[11] We report here a similarly dramatic effect for intramolecular reactions of chromium *siloxy*carbene compounds, but not for an *alkynoxy*carbene analogue.

The addition of 10 equiv of diphenylacetylene to complexes **1c**, **1d**, **1e**, **1f**, **1j**, and **1n** in hexane significantly enhanced the yield of the desired quinones (Table 1, entries 6, 9, 10, 12, 18, and 28, *vs* Table 2, entries 6, 13, 15, 16, 23, and 29). A survey of substitution patterns, chain lengths, and additives is presented in Figure 2 and Table 2. Regioselectivity was excellent for all intramolecular benzannulation reactions reported here, including those carried out in the absence of external alkyne: for complexes bearing substituted aromatic groups, only one of the two possible isomers of each product was detected. The yields of indanone products were relatively unaffected by the presence

Scheme 2



Scheme 3



of alkyne additive, the most dramatic response being a reduction from 16−18% in the absence of additive to 3−8% in the presence of diphenylacetylene for complex **1c**.[14] Intramolecular regiochemical control and the beneficial effect of PhCCPh additive were further demonstrated in annulation to 2-furyl and 2-propenyl moieties (complexes **8** and **10**, Scheme 2).

(a) Regiochemical Assignments. The structures of five representative quinones were determined by a variety of methods. Quinone products derived from disubstituted alkynols of each of the three chain lengths employed (n = 0−2) were characterized by X-ray crystallography (**2c**, the furyl derivative **9**, and **2v**). Quinone **2j** (from a terminal alkynol with n = 1) was analyzed by long-range ($^3J_{H,C}$) coupling (COLOC),[15] as was the crystallographically-characterized product **2c**, in order to confirm the results from the NMR method. The structure of **2j** was confirmed by comparison with the regioisomeric compound **12** prepared from a methoxycarbene complex and THP-protected alkynol (Scheme 3); the silicon-tethered and intermolecular reactions afforded complementary regioisomers that were readily distinguished by ^{1}H NMR spectroscopy. The structure of **12** was also substantiated by analysis of $^3J_{H,C}$ coupling patterns. Lastly, the structure of naphthoquinone **2n** (from a disubstituted alkynol with n = 1) was determined by comparison with products of an intermolecular reaction (Scheme 4). Thus, complex **13** and the methyl ether of 3-pentyn-1-ol afforded a 2.5:1 mixture of regioisomeric quinones, presumed to be **14** and **15**, respectively, from the steric selectivity "rule" common for standard benzannulation processes.[2a,d,g,8] The methyl ether of quinone **2n** was then shown to be identical to the minor isomer from the intermolecular reaction (**15**) by ^{13}C NMR. Details of these regiochemical analyses are given in the Experimental Section and supplementary material.

(b) Variations in Reaction Parameters. In contrast to intramolecular reactions of the siloxycarbene complexes alone (*vide supra*), benzannulation in the presence of external alkynes was sensitive to changes in alkynol chain length, but not in consistent fashion. Increasing the tether length in the reaction of *p*-tolyl-substituted complexes bearing a *disubstituted* alkyne fragment led to diminished yields: as n (Figure 2) was varied from 0 to 2, quinone yields are found to be 83%, 65%, and 50%, respectively (Table 2, entries 6, 29, and 38). However, either rendering the pendant alkyne monosubstituted or placing a *p*-methoxy group on the arylcarbene fragment led to maximal yields for the homopropargylic-derived substrates (n = 1): 40%, 60%, and 44% yields of quinone for complexes **1a**, **1j**, and **1p** (Table 2, entries 1, 23, and 36); and 39%, 55%, and 37% yields for complexes **1d**, **1o**, and **1w** (Table 2, entries 13, 33, and 40).

Entry 6 in Table 1 and entries 3−7 in Table 2 show that the activity of diphenylacetylene depends upon the additive−chromium ratio and is insensitive to overall concentration. Thus, at a constant concentration of complex **1c** (0.01 M), the beneficial effect of diphenylacetylene was found to depend on its concentration (equivalents of PhCCPh, yield of **2c**: 0, 33%; 2, 50%; 5, 70%; 10, 83%). In contrast, dilution of the reaction mixtures containing 5 and 10 equiv of PhCCPh by a factor of 10 (0.01 M Cr *vs* 0.001 M) did not affect the yields to a significant degree (Table 2, entries 4 *vs* 5 and 6 *vs* 7).

The intramolecular process appears to be tolerant of substitution at the alkynoxy carbinol center, an important substrate class for the synthesis of a variety of quinoid natural products. Thus, complexes **1l** (R^4 = Me), **1r** (R^4 = Et), and **1s** (R^4 = Et) underwent intramolecular benzannulation with roughly the same efficiency as their unsubstituted (R^4 = H) counterparts **1j**, **1c**, and **1e** under matching conditions (Table 2, entries 26 *vs* 23, 20 *vs* 12, and 21 *vs* 15.

The isolation of quinones **2a**, **2c**, **2j**, and **2n** in 40%, 83%, 60%, and 75% yields, respectively, compares favorably to the intramolecular benzannulation reactions of carbon-tethered alkynoxycarbene complexes of the same chain length, which proceed in poorer yields.[16] Comparisons between these systems are based on the assumption that the $-OCH_2CH_2CH_2-$ linkage is roughly equivalent in length and conformational flexibility to the $-OSiMe_2OCH_2-$ group. To determine the effect of added external alkyne on the reactions of a carbon-tethered complex, the *p*-tolylcarbene compound **16** was prepared from 5-hexyn-1-ol.[9a,d] In the absence of diphenylacetylene, **16** underwent benzannulation in THF in 38% yield (Scheme 5), exactly reproducing the reported result for the analogous phenylcarbene compound.[9a,d] A similar yield of hydroquinone acetate **17** was also obtained in hexane. The addition of 10 equiv of diphenylacetylene to the latter reaction, matching the optimum conditions for enhanced yield in the analogous silicon-tethered case (**1j**), had no effect on the yield of **17**.

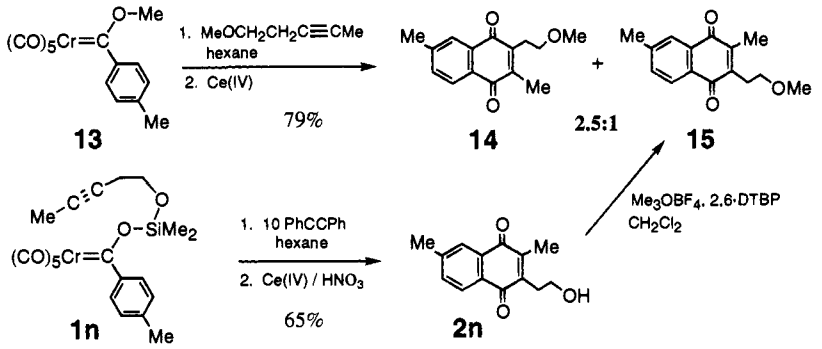
1-Hexyne and 3-hexyne exhibited the same type of effect as diphenylacetylene, but generally with less dramatic results. For example, the benzannulation reaction of complex **1n** in the presence of 10 equiv of 1-hexyne afforded a 54% yield of quinone **2n**, in contrast to a 27% yield without additive (Table 1, entry 28 *vs* Table 2, entry 30). In addition, 1-hexyne

(14) No information was obtained concerning the production of dehydrated indanone **4c** from complex **1c** and diphenylacetylene, since **4c** and the additive were not separated by column chromatography.

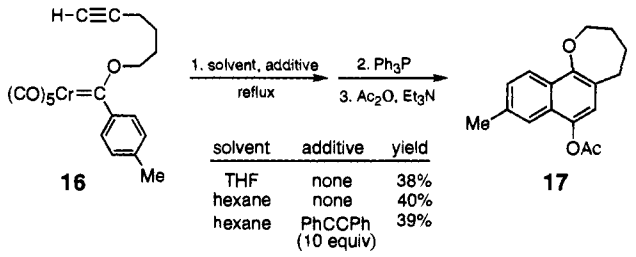
(15) Singh, S. B.; Cordingley, M. G.; Ball, R. G.; Smith, J. L.; Dombrowski, A. W.; Goetz, M. A. *Tetrahedron Lett.* **1991**, *32*, 5279−5282 and references therein.

(16) The intramolecular reaction of the alkoxycarbene complexes derived from 4-pentyn-1-ol, 4-hexyn-1-ol, 5-hexyn-1-ol, and 5-heptyn-1-ol (the same overall tether lengths to complexes **1a**, **1c**, **1j**, and **1n**) affords the corresponding annulated hydroquinones in 18%, 62%, 38%, and 62% yields, respectively: see refs 9a and 9d.

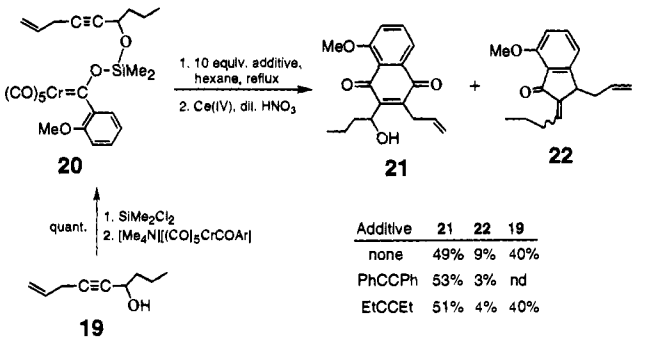
Scheme 4



Scheme 5

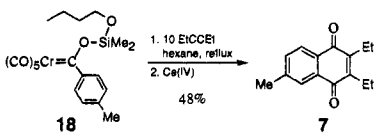


Scheme 6



competes with the tethered alkyne to a small extent, affording a 15% yield of quinone **7** deriving from intermolecular addition. 3-Hexyne performed better than both 1-hexyne and diphenylacetylene in this instance, providing a 75% yield of **2n** and 9% of **7** (Table 2, entry 32). Therefore, 3-hexyne occasionally may be preferred due to its convenient removal by evaporation, in spite of the possibility for its intermolecular reaction. When the tether is short (complex **1c**; $n = 0$), both 1- and 3-hexyne are less effective than diphenylacetylene (Table 2, entry 6 vs 9 and 12). Indeed, 1-hexyne provided no greater yield of **2c** than was obtained in the absence of additive (31% vs 33%), but the mass balance with respect to carbene was nearly doubled due to the production of the intermolecular benzannulation product **7** in 24% yield. 3-Hexyne gave a 51%:15% ratio of quinone–indanone products along with 19% of **7** when used in a 10-fold excess (Table 2, entry 12). Reducing the concentration of 3-hexyne from 0.10 (10 equiv) to 0.05 M (5 equiv) in reactions of both **1c** and **1n** gave very similar yields of both intra- and intermolecular products, but at 0.02 M (**1c** only) the yield of quinone was diminished while the extent of 3-hexyne incorporation remained the same (Table 2, entries 10–12). 3-Hexyne also had very little effect on quinone yields in the reactions of the terminal alkyne substrate **1j** ($n = 1$; Table 2, entry 24) and the complexes **1p** (entry 37) and **1v** (entry 39), which have longer tether lengths ($n = 2$). Thus, in most cases diphenylacetylene was the superior additive, giving higher yields of exclusively intramolecular benzannulation products. No incorporation of diphenylacetylene has been observed in intramolecular benzannulation reactions of silicon- or carbon-tethered complexes.

That siloxycarbene complexes are inferior to alkoxycarbene systems for *intermolecular* benzannulation was demonstrated with complex **18** bearing an *n*-butoxy group in place of an alkynoxy substituent. Reaction of **18** with 10 equiv of 3-hexyne provided the corresponding quinone **7** in only 48% yield (eq 4). Complex **18** and the methyl ether of 3-pentyn-1-ol afforded a 2.5:1 mixture of regioisomers **14** and **15** in 39% total yield (not shown), compared to 79% for the methoxycarbene analogue (Scheme 4). Note that the regioselectivity of siloxy- and methoxycarbene complexes (**18** and **13**) was identical in this case.



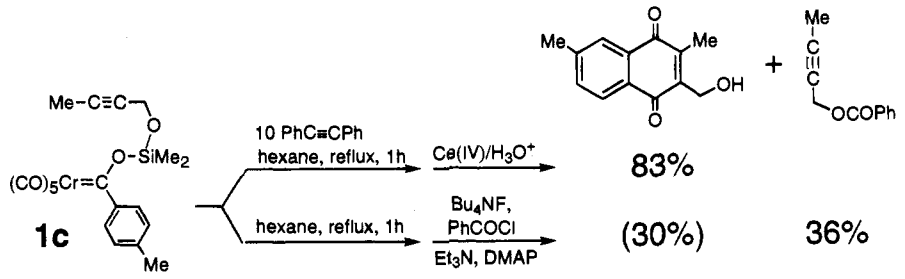
(4)

The beneficial action of added diphenylacetylene was manifested in nonpolar solvents (hexane and benzene), but it was completely suppressed in THF (Table 2, entries 2 and 27). The presence of 1 atm of carbon monoxide severely inhibited the action of diphenylacetylene, reducing the yield of **2c** from 83% to 45% for the reaction of **1c** in the presence of 10 equiv of PhCCPh (Table 2, entry 8 *vs* 6); in the absence of both PhCCPh and CO, **2c** was produced in 33% yield (Table 1, entry 6). We have made similar observations with manganese siloxycarbene complexes, for which CO and PPh_3 were not effective additives.[11]

The intramolecular benzannulation reactions of substrates bearing long-chain substituents at the alkyne terminus, which gave the highest yields in the absence of external alkyne (*vide supra*), were found to be *insensitive* to the addition of diphenylacetylene or 3-hexyne (**2g**, **2i**; Table 2, entries 17–19 *vs* Table 1, entries 13 and 15). A similar resistance to added alkyne was observed in the conversion of siloxycarbene complex **20** to quinone **21**, a precursor to the naphthoquinone antibiotic (*dl*-deoxyfrenolicin (Scheme 6).[9a,b] Compound **21** has been prepared by Semmelhack and co-workers in 33% yield from the pentacarbonylchromium acylate, by an intramolecular benzannulation route requiring four steps to install and remove an ether linkage to achieve the correct tether length.[9a,b] We obtained **21** by a one-pot procedure in 49–53% yield[17] from the carbene acylate salt and alkynol **19**, under a variety of conditions as noted in Scheme 6. Also isolated were small amounts of

(17) A 5% and 9% yield of the ketone produced by overoxidation in workup is included for reactions done in the presence of diphenylacetylene and 3-hexyne, respectively.

Scheme 7



indanone **22** (3−9%) and large amounts of recovered **19** (40%). Reactions performed in the absence of additive and in the presence of diphenylacetylene or 3-hexyne gave very similar results. The quinone derived from intermolecular incorporation of 3-hexyne was not detected.

The fate of alkynol in a tethered reaction was probed with **1c** (Scheme 7). In the absence of additive, complex **1c** was heated at reflux in hexane until the carbonyl ligand IR stretching bands of the starting complex disappeared (1 h). The crude reaction mixture was then treated with excess benzoyl chloride, triethylamine, and tetrabutylammonium fluoride to afford the benzoate ester of the starting alkynol (2-butyn-1-ol) in 36% isolated yield.

The effects of *o*- and *p*-methoxy substituents on the carbene aryl fragment were investigated relative to *p*-methyl analogues. The yields of naphthoquinones from three sets of complexes in the presence of diphenylacetylene were compared: **1c** (*p*-Me, 83%) *vs* **1d** (*p*-OMe, 39%) *vs* **1e** (*o*-OMe, 62%); **1v** (*p*-Me, 50%) *vs* **1w** (*p*-OMe, 37%) *vs* **1x** (*o*-OMe, 65%); and **1n** (*p*-Me, 65%) *vs* **1o** (*p*-OMe, 55%) *vs* **1u** (*o*-OMe, 59%). Two additional comparisons of *p*-Me- and *o*-OMe-substituted complexes were performed: **1g** (51%) *vs* **1i** (49%); and **1j** (60%) *vs* **1t** (41%). The *p*-OMe substituent was found to consistently inhibit the benzannulation process, whereas *o*-OMe groups had variable effects, in one case giving higher yields. A similar trend for complexes **1c** *vs* **1d** *vs* **1e** was also observed in the absence of additive (Table 1, entries 6, 9, and 10). It is our experience in the synthesis of other naphthoquinones that arylcarbene complexes bearing *p*-OMe groups respond less favorably to the addition of additives than *p*-Me, *o*-Me, *o*-OMe, and *m*-OMe analogues.[18]

(c) Kinetics. Kinetics measurements were performed by monitoring the disappearance of starting siloxycarbene complexes in a sealed, heated IR cell. Figure 3 shows the resulting linear plots of the logarithm of the absorbance of the two CO bands of the starting siloxycarbene complexes (top set, 1956 cm^{-1}; bottom set, 2062 cm^{-1}) as a function of time. The processes examined were the intramolecular reaction of acetylenic siloxycarbene complex **1n** in the presence and absence of 3-hexyne, and the intermolecular reaction of the butyloxy siloxycarbene complex **18** with 3-hexyne, all at identical concentrations in hexane at 64.9 ± 0.5 °C. Averaging the results of at least two runs for each reaction showed all of these processes to proceed at the same rate within experimental error: **1n** alone, $3.9 \pm 1.1 \times 10^{-4}$ s^{-1}; **1n** with 10 equiv of 3-hexyne, $4.5 \pm 0.9 \times 10^{-4}$ s^{-1}; **18** with 10 equiv of 3-hexyne, $4.0 \pm 1.0 \times 10^{-4}$ s^{-1}.

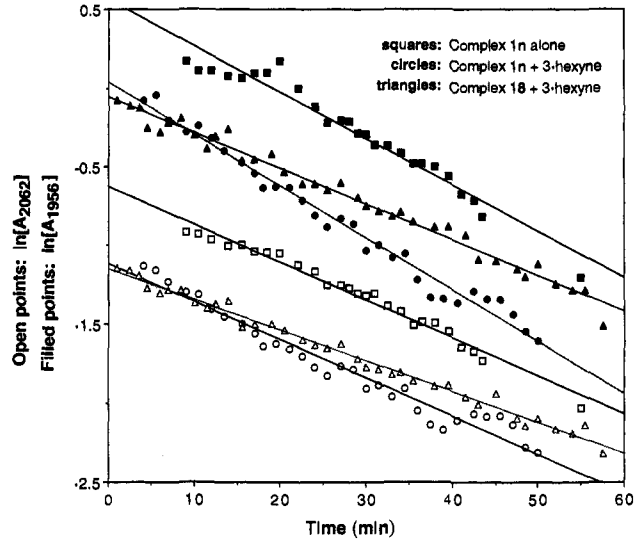


Figure 3. Disappearance of siloxycarbene complexes as a function of time as described in the text; $[Cr]_{start} = 0.10$ M, $T = 64.9 \pm 0.2$ °C.

Discussion

The tethered siloxycarbene strategy represents a convenient method for the regioselective incorporation of acetylenic alcohols into quinoid products. We focus here on issues of mechanism centering on the effect of alkyne additives. The following discussion is based upon the proposals of Wulff and co-workers concerning the "allochemical" effect of added alkyne substrates in the intermolecular benzannulation reactions.[3b] Since the modulating alkynes in the present intramolecular process are not actually substrates, we will term their action a "**xenochemical**" effect, from the Greek "ceno" ("foreign").

The allochemical phenomenon is manifested by differing ratios of quinone and indanone products. In contrast, siloxycarbene complex intermediates decompose rather than annulate in the absence of alkyne. This may be due in part to the relative instability of Fischer carbene systems bearing Lewis acidic oxygen substituents with respect to "standard" alkoxycarbene compounds.[19] Furthermore, the intrinsic efficiency of indanone production is low in intramolecular reactions and does not seem to be improved by donor solvents, donor functionality on the carbene aryl group, or external additives. Indeed, carbon-tethered reactions of alkoxycarbene compounds are not reported to provide such products at all.[9a-d,20] Thus, the xenochemical effect in intramolecular siloxycarbene reactions has the consequence of increasing the overall mass balance and selectivity by boosting the yield of quinone products.

The following conclusions and hypotheses concerning the mechanism of benzannulation and the xenochemical effect can be made.

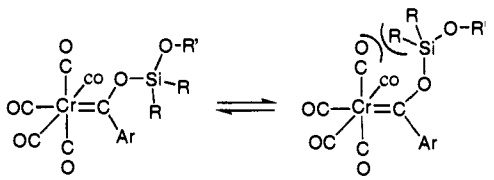
(1) Kinetics measurements demonstrated equivalent rates of intermolecular and intramolecular benzannulation, the latter in the presence and absence of external alkyne. In addition, the rates of intramolecular reactions appear to be unaffected by

(18) Balzer, B. L.; Finn, M. G., unpublished results.

(19) Sabat, M.; Gross, M. F.; Finn, M. G. *Organometallics* **1992**, *11*, 745−751.

(20) Aminocarbene complexes with tethered alkyne groups afford indene derivatives selectively: see ref 9e.

Scheme 8



s-trans **s-cis**

changes in concentration. These observations are consistent with rate-limiting CO loss that is dissociative in character: neither external nor tethered alkyne is involved. Similar findings have been reported for the reaction of diphenylacetylene with $(CO)_5Cr(OMe)(Ph)$[21] and for CO dissociation processes of tungsten carbene complexes.[22]

(2) The yield of **2c** from **1c** appears to be sensitive to the additive−Cr ratio, but not to dilution of the reaction mixture at a constant value of additive−Cr. This is in contrast to reactions of methoxycarbene complexes, which respond to changes in the alkyne concentration, whether by overall dilution or alteration of the alkyne−Cr ratio.[3b,23] If quinone is produced by a sequence of steps that is first-order in additive (A) and siloxycarbene complex (C), then a *bimolecular* pathway for siloxycarbene decomposition would account for the observed [A]/[C] dependence of quinone formation relative to decomposition:

$$\frac{\text{quinone}}{\text{decomposition}} \propto \frac{[A][C]}{[C]^2} \propto \frac{[A]}{[C]}$$

The isolation of significant quantities of benzil derivatives is consistent with a bimolecular decomposition pathway, but dilution of reaction mixtures in the absence of additive does not enhance the yields of quinones. Bimolecular decomposition processes have been suggested for two methoxycarbene systems.[24,25]

(3) Following CO loss, the tethered alkyne may either interact with the coordinatively unsaturated Cr center[25] or undergo direct insertion into the Cr=C bond.[4e] For the chain lengths studied here, either step requires an *s-cis* conformation about the carbenoxy C−O bond, which is expected to have the partial double-bond character that is common to Fischer carbene systems. The sterically less demanding *s-trans* structure should be increasingly favored for larger oxygen substituents, consistent with the progressive failure of the intramolecular benzannulation reaction as the dialkylsilicon center is changed from $SiMe_2$ to $SiEt_2$ to $Si(i\text{-}Pr)_2$ (Scheme 8).

(4) The structures of the regioisomers produced in the presence or absence of additive are consistent with the currently accepted mechanism for the benzannulation process, in which alkyne insertion gives rise to a vinylcarbene intermediate.[3,4] The silicon tether directs the insertion step to override the intrinsic regiochemical bias of the reaction corresponding to placement of the larger alkyne substituent nearer to chromium in the cases for which R^1 = H.[2a,d,g,8] The putative vinylcarbene structure **24** is shown in Scheme 9.[26]

(5) The isolation of naphthoquinones from intramolecular reactions using terminal alkynols in 40−60% yield represents a dramatic improvement on the reactions of analogous tethered alkoxy- and aminocarbene complexes[9] and a carbon-tethered methoxycarbene complex.[27] The poor yields have been ascribed to poor stabilization by the terminal H atom of developing carbonium ion character upon nucleophilic attack at the carbene carbon.[9d] The same consideration should apply to the analogous siloxycarbene reactions, in which case yields should also be low and should not respond to the addition of alkyne additives. The observed xenochemical effect renders this rationale either incomplete or incorrect, as would be suggested by recent calculations concerning the mechanism of alkyne insertion.[4e] The failure of intramolecular reactions of terminal alkynes for both carbon- and silicon-tethered systems in the absence of additive may instead be explained in terms of the stability of intermediates formed *after* alkyne insertion, as discussed below. It should also be noted that the increased production of five-membered-ring products observed for intermolecular reactions of propargyl ethers[28] is not found here for tethered propargyl substrates.

(6) A summary of the steps involved in intramolecular benzannulation and the xenochemical effect is shown in Scheme 9, which is derived from the proposals of Wulff and co-workers.[3] Intramolecular benzannulation of siloxycarbene complex **1** is initiated by CO loss (*vide supra*) to give intermediate **23**, followed by alkyne insertion to afford the vinylcarbene species **24**; the latter process may occur *via* precoordination of the pendant alkyne to the vacant coordination site.[25] Alternatively, **1** can undergo decomposition or reaction with external alkyne to give **7**. The relative rates of these various processes control the outcome. That external alkyne acts by capture of a vinylcarbene intermediate **24** rather than unsaturated complex **23** is supported by the following four considerations.

(a) Competitive intermolecular benzannulation must occur via adduct **28**.[25] If both the xenochemical effect and intermolecular reaction proceed through **28**, one would expect all effective alkyne additives to undergo at least a small amount of intermolecular benzannulation as well. While this is true for 1- and 3-hexyne, diphenylacetylene is an excellent xenochemical additive that completely resists incorporation into quinone products in this system. Diphenylacetylene is an active substrate (indeed, the first substrate[1]) for insertion reactions with standard alkoxycarbene complexes.[21,23,29]

(b) Coordination of the pendant alkyne to the unsaturated Cr site of **23** should be much faster than complexation of an external ligand. Furthermore, the relative rates of intra- and intermolecular trapping should be sensitive to the steric nature of the external alkyne. Thus, it is difficult to explain the

(21) (a) Fischer, H.; Mühlemeier, J.; Märkl, R.; Dötz, K. H. *Chem. Ber.* **1982**, *115*, 1355−1362; rates are reported that are similar (within a factor of 10) to those found here. (b) For kinetics measurements on the carbene insertion reactions of ynamines and cyanamides, which proceed by a different mechanism, see: Schneider, K. J.; Neubrand, A.; van Eldik, R.; Fischer, H. *Organometallics* **1992**, *11*, 267−269. Fischer, H.; Dötz, K. H. *Chem. Ber.* **1980**, *113*, 193−202.

(22) Bell, S. E. J.; Gordon, K. C.; McGarvey, J. J. *J. Am. Chem. Soc.* **1988**, *110*, 3107−3112.

(23) Chan, K. S.; Peterson, G. A.; Brandvold, T. A.; Faron, K. L.; Challener, C. A.; Hyldahl, C.; Wulff, W. D. *J. Organomet. Chem.* **1987**, *334*, 9−56.

(24) Casey, C. P.; Anderson, R. L. *J. Chem. Soc., Chem. Commun.* **1975**, 895−896.

(25) Dötz, K. H.; Schäfer, T.; Kroll, F.; Harms, K. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1236−1238.

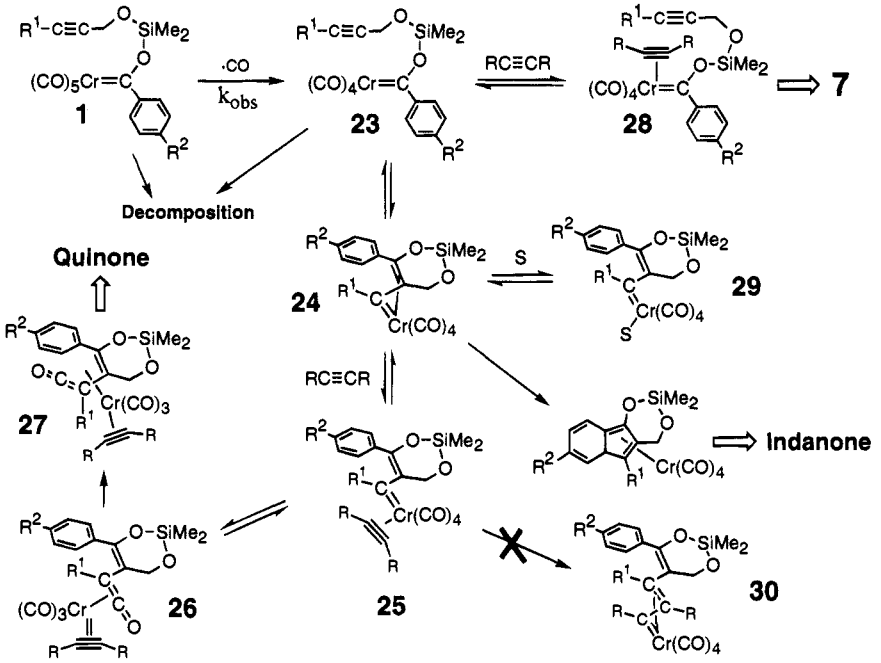
(26) Since furans are thought to arise from (*Z*)-vinylcarbene insertion intermediates,[3a] and intramolecular benzannulation reactions (both silicon- and carbon-tethered) do not give furan products,[29a,40] it is possible that intramolecular alkyne insertion is selective for (*E*)-vinylcarbenes such as **24**. Note that other reactions of tethered alkynes have also been reported to occur through analogous vinylcarbene intermediates.[9,27,31] However, certain *inter*molecular reactions have been found to afford products derived from both putative vinylcarbene isomers.[3a,32,41]

(27) Wulff, W. D.; Xu, Y.-C. *Tetrahedron Lett.* **1988**, *29*, 415−418.

(28) (a) Semmelhack, M. F.; Jeong, N. *Tetrahedron Lett.* **1990**, *31*, 605−608. (b) Semmelhack, M. F.; Jeong, N.; Lee, G. R. *Tetrahedron Lett.* **1990**, *31*, 609−610.

(29) (a) Dötz, K. H. *J. Organomet. Chem.* **1977**, *140*, 177−186. (b) Foley, H. C.; Strubinger, L. M.; Targos, T. S.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1983**, *105*, 3064−3073.

Scheme 9



observation that diphenylacetylene is at least as active an additive as 1- or 3-hexyne, if the xenochemical effect results from external capture of **23**.

(c) An *o*-OMe substituent on the arylcarbene fragment can be expected to coordinate to the vacant *cis* site of **23**.[3b] Since *o*-methoxyphenyl siloxycarbene complexes demonstrate an efficient xenochemical effect, the external alkyne additive is not likely to bind to **23**.

(d) Long-chain or bulky groups at the alkyne terminus (R^1) served to inhibit the action of alkyne additives. This is consistent with external alkyne action by capture of **24** and not **23**, since only in the former is R^1 near the metal center, and can thereby affect alkyne coordination.

(7) The recovery of substantial quantities of unreacted alkynol upon complete consumption of complex **1c** in the absence of additive (Scheme 7) suggests that decomposition occurs before the tethered alkyne attacks the carbene center, either from the starting structure **1** or tetracarbonyl species **23**. If external alkyne does not preferentially intercept **23**, as discussed above, then intramolecular alkyne insertion must be *rapidly reversible* in order for alkyne additives to have an effect on the relative rates of decomposition *vs* product formation. Therefore, the quinone-forming pathway is under thermodynamic (equilibrium) control until an irreversible step is reached, which is proposed to be isomerization of **26** to the η^4-vinylketene[5] intermediate **27**.

Vinylcarbene **24** (Scheme 9) can either undergo annulative ring closure to give indanone or CO insertion. As originally suggested by Wulff and co-workers, bound alkyne may stabilize η^2-vinylketene intermediates of the type **26** by switching from two-electron donation (structure **25**) to four-electron donation (indicated by the "double" bond connecting Cr and alkyne in **26**).[3b] The metal center thereby retains an 18-electron configuration and the Cr–alkyne interaction is greatly strengthened.[30] This may increase the rate or the equilibrium constant of CO insertion and thereby favor the production of quinone. Alternatively for the siloxycarbene system, a coordinated alkyne can simply protect the vinylcarbene **24** against decomposition. Two-alkyne annulation[27,31] *via* **30** is apparently also disfavored with respect to CO insertion from intermediate **25**.

The reversible nature of alkyne insertion has been previously suggested.[32] However, it has also been proposed that alkyne insertion is irreversible to account for the configurational stability of vinylketene intermediates in an intermolecular benzannulation reaction of a methoxycarbene complex.[3a] While it is possible that siloxy- and alkoxycarbene systems behave differently in this regard, a unifying hypothesis is also available: alkyne insertion is rapidly reversible, but the formation of η^4-coordinated vinylketene is not, as shown in Scheme 9. A reversible vinylcarbene–vinylketene transformation has been reported for iron.[5m]

(8) Two-electron donors have a more profound effect on the intramolecular reactions of siloxycarbene compounds than on the intermolecular reactions of alkoxycarbene complexes. For example, whereas increasing alkyne concentrations in the presence of THF or carbon monoxide results in observable allochemical effects for methoxycarbene systems,[3b] these ligands eliminate such effects in the present work. Thus, diversion of the vinylcarbene intermediate **24** to the solvent- or CO-bound intermediate **29** diminishes the effective concentration of **25**, allowing decomposition to take over. Although donor solvents are known to favor the formation of indanones from methoxycarbene complexes,[23] no such effect is observed here.

(9) Although yields are lower for siloxycarbene complexes bearing terminal alkynes, a definite xenochemical effect is observed, whereas the low-yield benzannulation reaction of the carbon-tethered alkynoxycarbene complex **16** does not respond to the addition of diphenylacetylene (Scheme 5). We suggest that a contributing factor toward the poor performance of terminal alkynols in intramolecular reactions may be found in the relative stabilities of the vinylcarbene intermediates **24** (Scheme 9). Vinylcarbene species lacking a heteroatom substituent directly bound to the carbene carbon are known to be

(30) Birdwhistell, K. R.; Tonker, T. L.; Templeton, J. L. *J. Am. Chem. Soc.* **1987**, *109*, 1401–1407.

(31) (a) Xu, Y.-C; Challener, C. A.; Dragisich, V.; Brandvold, T. A.; Peterson, G. A.; Wulff, W. D.; Williard, P. G. *J. Am. Chem. Soc.* **1989**, *111*, 7269–7271. (b) See also ref 41a and: Bao, J.; Dragisich, V.; Wenglowski, S.; Wulff, W. D. *J. Am. Chem. Soc.* **1991**, *113*, 9873–9875.

(32) Yamashita, A.; Scahill, T. A. *Tetrahedron Lett.* **1982**, *23*, 3765–3768.

highly reactive,[27,31a,7h,33] and those in which R^1 = H should be even further destabilized relative to those in which R^1 = alkyl.[34] This situation arises only for the intramolecular benzannulation of terminal alkynes since intermolecular processes proceed with the opposite regioselectivity. The implication is that an external alkyne is able to capture vinylcarbene species such as **24** derived from silicon-tethered, but not carbon-tethered, terminal alkynols; this possibility is currently being tested.

The poisoning of the xenochemical effect by a *p*-methoxy arylcarbene substituent resembles observations by Wulff and co-workers concerning the influence of *p*-OMe on the allochemical phenomenon. Their suggestion that resonance donation from the *p*-OMe group makes for an electron-rich vinylcarbene intermediate that does not undergo reaction with another equivalent of alkyne may be applicable here as well.

The results of further studies that take advantage of the unique mechanistic window on the benzannulation process provided by the xenochemical effect will be reported in due course.

Experimental Section

General Methods. ^{1}H and ^{13}C NMR spectra were recorded at 300 and 75.2 MHz, respectively, on either a GE GN-300 or QE-300 instrument referenced to residual protons in the solvent. Long-range ^{1}H−^{13}C coupling experiments were performed on a GE Omega 500 MHz instrument. IR spectra were recorded on a Mattson Cygnus 1000 instrument using 0.10 mm CaF_2 solution cells. THF, hexane, and benzene were purified by distillation from sodium benzophenone ketyl and CH_2Cl_2 was purified by distillation from P_4O_{10}. All alkynols except 4-hexyn-1-ol[35] and 1-nonen-4-yn-5-ol,[36] **19**, were purchased from Farchan and purified by Kugelrohr distillation prior to use.[37] All other reagents were purchased from commercial suppliers and used as received. All manipulations involving siloxycarbene complexes were conducted under dry nitrogen or argon atmosphere, either in a Vacuum-Atmosphere glovebox or using standard Schlenk techniques. All yields are reported for spectroscopically pure compounds isolated by flash chromatography on Kieselgel-60 (230−400 mesh, EM Science), packed as a slurry; for all samples mixtures of ethyl acetate and light petroleum ether (bp 40−60 °C) were used. Isolated yields are reported as the average of two or more runs; yields of individual runs were reproducible within 5%. Elemental analyses were performed at the University of Virginia on a Perkin-Elmer Model 2400 CHN analyzer, using acetanilide as the calibration standard, or by Desert Analytics, Tuscon, AZ. All crystalline products gave satisfactory C,H,N analyses. However, oils repeatedly purified by column chromatography and free of impurities by NMR and capillary GLC gave inconsistent results.

Syntheses. Pentacarbonylchromium acylate complexes, $[(CO)_5Cr(COR)][NMe_4]$ (R = Ph, *p*-Me Ph, *p*-OMe Ph *o*-OMe), were prepared from $Cr(CO)_6$ and the appropriate lithium reagent by the Fischer method[38] and were recrystallized from CH_2Cl_2. Alkynoxysilyl chlorides and siloxycarbene complexes were prepared as described below. The alkynoxycarbene complex **16**[9a,d] and the methoxycarbene complex shown in Scheme 3 were prepared according to literature methods.

Reactions of Siloxycarbene Complexes. Typical Experimental Procedure Described for Complex 2c. 2-Butyn-1-ol (500 mg, 7.1 mmol) was added dropwise at room temperature to neat dichlorodimethylsilane (9.10 g, 70.5 mmol). Immediate removal of HCl and excess $SiMe_2Cl_2$ *in vacuo* provided $SiMe_2(OCH_2CCCH_3)Cl$ in quantitative yield which required no additional purification. Preparation of **1c** was accomplished by dropwise addition of a solution of $SiMe_2(OCH_2CCCH_3)Cl$ (84 mg, 0.52 mmol) in 3 mL of CH_2Cl_2 to a stirred solution of $[(CO)_5Cr(CO\text{-}p\text{-}MePh)][NMe_4]$ (200 mg, 0.52 mmol) in 20 mL of CH_2Cl_2. After several minutes, NMe_4Cl was removed by filtration and the solvent was removed *in vacuo* to give **1c** in quantitative yield. The complex was taken up in 50 mL of hexane ([Cr] = 0.01 M) and diphenylacetylene (922 mg, 5.2 mmol, 10.0 equiv) was added. The reaction mixture was heated to reflux with stirring and monitored by IR spectroscopy until the carbonyl ligand stretching bands of the starting siloxycarbene complex disappeared (≈1 h). The reaction mixture was allowed to cool to room temperature under inert atmosphere and the solvent was removed by rotary evaporation in air. The residue was taken up in 40 mL of Et_2O and treated with 10 mL of a 0.5 M solution of ceric ammonium nitrate in 0.1 N aqueous nitric acid (10 equiv). The combined aqueous and organic layers were stirred vigorously for 10 min. The aqueous phase was then extracted with Et_2O (3 × 25 mL), and the combined organic extracts were dried ($MgSO_4$) and concentrated. The products were separated by flash chromatography using a 65:35 petroleum ether−ethyl acetate mixture. The diphenylacetylene eluted rapidly and was recovered quantitatively followed by **2c** in 83% yield and **3c** in 3% yield.

Nonoxidatitive Workup Procedures. Following the completion of reactions of complexes **1j** and **1n**, the solvent was removed by rotary evaporation in air. In each case the residue was taken up in 50 mL of Et_2O and Bu_4NF (3.0 molar equiv with respect to starting carbene complex as a 1.0 M solution in THF) was added dropwise with stirring. After 15 min, 15 equiv of MeOH was added all at once followed immediately by 15 equiv of Me_3SiCl (the use of MeOH/Me_3SiCl as an acid source gave slightly higher yields then dilute HCl) and the mixture was allowed to stir an additional 15 min. The volatile components were removed *in vacuo* and the residue was taken up in 15 equiv of Ac_2O and 20 equiv of pyridine. After 10 h, the products were isolated by column chromatography after evaporation of the volatile components under high vacuum. The reactions of complex **16** (Scheme 5) were subjected to workup conditions similar to those used in ref 9.

Kinetics. Hexane solutions of complex **1n** alone, **1n** plus 10 equiv of 3-hexyne, and complex **18** plus 10 equiv of 3-hexyne, each 0.010 M in chromium, were transferred at room temperature to a jacketed IR cell with cadmium telluride windows (Wilmad Glass Co., Model 118-1). The cell was then connected to a thermostat-controlled Haake A82 recirculating ethylene glycol/water bath at 64.5 ± 0.2 °C. After a 2−3 min equilibration time, IR spectra of the CO stretching region were recorded every 2−4 min until the starting carbene complexes (ν_{CO} = 2062, 1956 cm^{-1}) had disappeared and the formation of $Cr(CO)_6$ (ν_{CO} = 1986 cm^{-1}) was complete. Plots of ln(absorbance) (corrected for baseline absorption) of both starting material peaks vs time were linear through at least two reaction half-lives; past that point the low intensities of the monitored peaks resulted in widely scattered data. Slopes and correlation factors (R^2) for each run are presented in Table 3.

Table 3. Kinetics of Siloxycarbene Complex Disappearance Monitored at the Indicated Wavelengths

reaction	run no.	slope (2062 cm^{-1}), 10^{-4} s^{-1}	R^2	slope (1956 cm^{-1}), 10^{-4} s^{-1}	R^2
1q alone	1	3.10	0.98	3.62	0.95
	2	4.02	0.98	4.90	0.95
1q + 3-hexyne	1	4.63	0.97	5.52	0.96
	2	3.38	0.95	4.25	0.95
	3	4.02	0.96	5.50	0.98
18 + 3-hexyne	1	3.23	0.99	3.78	0.98
	2	4.17	0.99	4.92	0.97

Regiochemical Assignments. X-ray Crystallography. Crystals of quinones **2c**, **2v**, and **9** were obtained by slow evaporation from mixtures of CH_2Cl_2 and pentane. X-ray diffraction analysis established the expected structure of these compounds. ORTEP diagrams, tables of coordinates, and experimental details of the crystallographic analyses are given in the supplementary material.

Long-Range ^{1}H,^{13}C-NMR Coupling (COLOC). Compound **12**, the regioisomer of **2j**, was prepared as outlined in Scheme 3. A

(33) Korkowski, P. F.; Hoye, T. R.; Rydberg, D. B. *J. Am. Chem. Soc.* **1988**, *110*, 2676−2678.

(34) For example, $(CO)_5W{=}C(Ph)_2$ is significantly more stable than $(CO)_5W{=}C(H)(Ph)$—see the results of Casey et al. [Casey, C. P.; Polichnowski, S. W.; Shusterman, A. J.; Jones, C. R. *J. Am. Chem. Soc.* **1979**, *101*, 7282−7292] compared to those of Casey and Burkhardt [Casey, C. P.; Burkhardt, T. J. *J. Am. Chem. Soc.* **1973**, *95*, 5833−5834].

(35) 4-Hexyn-1-ol was prepared by deprotonating the THP ether of 4-pentyn-1-ol with *n*-butyllithium followed by alkylation with methyl triflate.

(36) Prepared as in ref 9a, except that NaI (1 equiv) was used instead of CuI.

(37) 2-Decyn-1-ol was used as received.

(38) (a) Aumann, R.; Fischer, E. O. *Chem. Ber.* **1960**, *101*, 954−966. (b) Hegedus, L. S.; McGuire, M. A.; Schultze, L. M. *Org. Synth.* **1987**, *65*, 140−144.

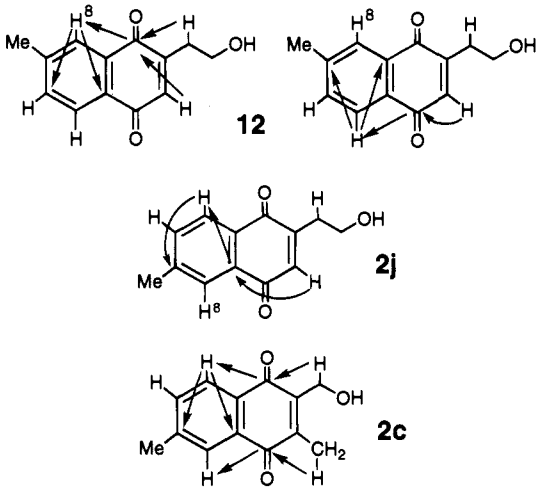


Figure 4. Long-range NMR correlations establishing the structures of **12** (top), **2j** (middle), and **2c** (bottom). No information involving the carbonyl resonances of **2j** could be obtained because they are not resolved in the ^{13}C NMR spectrum.

comparison of ^1H NMR spectra for **2j** and **12** (listed below) showed a difference of 0.12 ppm for H8 (7.72 ppm vs 7.84 ppm; assigned by the $^1H,^{13}C$-correlated 2D spectrum, see Figure 4). These signals were clearly resolved in the NMR spectrum of a mixture of the two compounds, confirming that **2j** and **12** are not identical and are therefore regioisomers. The structures of **12** and **2j** were also assigned by long-range $^1H,^{13}C$-correlated spectroscopy (COLOC), optimized for three-bond coupling ($^3J_{CH}$ = 7−10 Hz).[15] To verify the accuracy of the COLOC technique, compound **2c** was subjected to the same analysis, with results in agreement with its crystal structure determination. The COLOC correlations, which were obtained from data given in the supplementry material,[39] are summarized in Figure 4.

Product Characterization. 2a: ^1H NMR ($CDCl_3$, δ) 7.98 (d, J = 7.8 Hz, 1 H), 7.88 (s, 1 H), 7.54 (d, J = 7.8 Hz, 1 H), 6.98 (t, J = 1.5 Hz, 1 H), 4.68 (d, J = 1.5 Hz, 2 H), 2.50 (s, 3 H); ^{13}C NMR ($CDCl_3$) 185.3, 148.9, 145.3, 134.5, 133.3, 132.0, 129.8, 126.7, 126.5, 60.2, 21.9; IR ($CDCl_3$, cm^{-1}) 1664, 1629, 1603.

2b: ^1H NMR ($CDCl_3$, δ) 8.06−8.01 (m, 2 H), 7.71−6.68 (m, 2 H), 4.70 (s, 2 H), 2.23 (s, 3 H); ^{13}C NMR ($CDCl_3$, δ) 186.0, 185.2, 144.8, 142.5, 133.9, 133.7, 131.9, 131.7, 126.5, 126.2, 57.9, 12.2; IR (CH_2Cl_2, cm^{-1}) 1666, 1624, 1596. Anal. Calcd for $C_{12}H_{10}O_3$: C, 71.28; H, 4.98. Found: C, 71.20; H, 5.40.

2c: ^1H NMR ($CDCl_3$, δ) 7.90 (d, J = 7.8 Hz, 1 H), 7.82 (s, 1 H), 7.48 (d, J = 7.8 Hz, 1 H), 6.76 (br s, 1 H, D_2O exchangeable), 4.72 (s, 2 H), 2.46 (s, 3 H), 2.21 (s, 3 H); ^{13}C NMR ($CDCl_3$, δ) 186.0, 185.4, 145.2, 144.7, 141.9, 134.5, 131.8, 129.4, 126.9, 126.4, 58.0, 21.8, 12.2; IR ($CDCl_3$, cm^{-1}) 1665, 1622, 1602. Anal. Calcd for $C_{13}H_{12}O_3$: C, 72.21; H, 5.59. Found: C, 72.14; H, 5.91.

2d: ^1H NMR ($CDCl_3$, δ) 8.01 (d, J = 8.7 Hz, 1 H), 7.51 (d, J = 2.7 Hz, 1 H), 7.17 (dd, J = 2.7 and 8.7 Hz, 1 H), 4.68 (s, 2 H), 3.94 (s, 3 H), 2.76 (br s, 1 H), 2.22 (s, 3 H); ^{13}C NMR ($CDCl_3$, δ) 185.4, 185.2, 164.1, 143.9, 142.8, 134.0, 128.7, 125.3, 120.3, 109.8, 58.1, 55.9, 12.2; IR (CH_2Cl_2, cm^{-1}) 1665, 1651, 1596. Anal. Calcd for $C_{13}H_{12}O_4$: C, 67.23; H, 5.21. Found: C, 67.37; H, 4.84.

2e: ^1H NMR ($CDCl_3$, δ) 7.66 (d, J = 7.8 Hz, 1 H), 7.59 (t, J = 7.8 Hz, 1 H), 7.22 (d, J = 7.8 Hz, 1 H), 4.60 (s, 2 H), 3.94 (s, 3 H), 3.05 (br s, 1H), 2.15 (s, 3 H); ^{13}C NMR ($CDCl_3$, δ) 185.4, 159.4, 144.4, 142.1, 134.8, 134.1, 119.4, 119.1, 117.5, 58.0, 56.3, 11.8; IR ($CDCl_3$, cm^{-1}) 1652, 1587. Anal. Calcd for $C_{13}H_{12}O_4$: C, 67.23; H, 5.21. Found: C, 67.20; H, 4.94.

2f: ^1H NMR ($CDCl_3$, d) 8.02 (d, J = 7.8 Hz, 1 H), 7.90 (s, 1 H), 7.56 (d, J = 7.8 Hz, 1 H), 7.45 (m, 3 H), 7.29 (m, 2 H), 4.49 (s, 2 H), 2.50 (s 3 H); ^{13}C NMR ($CDCl_3$, d) 186.8, 184.8, 146.2, 145.4, 142.9, 134.6, 131.8, 129.7, 129.1, 128.1, 127.1, 126.3, 59.3, 21.9; IR (CH_2Cl_2, cm^{-1}) 1665, 1603. Anal. Calcd for $C_{18}H_{14}O_3$: C, 77.68; H, 5.07. Found: C, 77.94; H, 4.91.

2g: ^1H NMR ($CDCl_3$, δ) 7.83 (d, J = 7.8 Hz, 1 H), 7.75 (s, 1 H), 7.39 (d, J = 7.8 Hz, 1 H), 4.59 (s, 2 H), 3.24 (br s, 1 H), 2.60 (t, J = 6.9 Hz, 2 H), 2.40 (s, 3 H), 1.44−1.21 (m, 10 H), 0.81 (t, J = 6.9 Hz, 3 H); ^{13}C NMR ($CDCl_3$, δ) 186.1, 185.1, 148.2, 144.7, 142.4, 134.1, 131.8, 129.4, 126.6, 126.1, 57.5, 31.6, 30.0, 29.7, 28.9, 26.2, 22.5, 21.7, 13.9; IR (CH_2Cl_2, cm^{-1}) 1663, 1653, 1601. Anal. Calcd for $C_{19}H_{24}O_3$: C, 75.97; H, 8.05. Found: C, 75.86; H, 7.86.

2h: ^1H NMR ($CDCD_3$, δ) 7.95 (d, J = 8.4 Hz, 1 H), 7.46 (d, J = 2.7 Hz, 1 H), 7.13 (dd, J = 2.7 and 8.4 Hz, 1 H), 4.62 (s, 2 H), 3.91 (s, 3 H), 2.62 (t, J = 6.9 Hz, 2 H), 1.46−1.25 (m, 10 H), 0.85 (t, J = 6.9 Hz, 3 H); ^{13}C NMR ($CDCl_3$, δ) 185.6, 185.1, 164.0, 147.9, 142.6, 134.0, 128.5, 125.3, 120.2, 109.7, 57.9, 55.8, 31.7, 30.1, 29.8, 29.0, 26.2, 22.5, 14.0; IR (CH_2Cl_2, cm^{-1}) 1665, 1647, 1595. Anal. Calcd for $C_{19}H_{24}O_4$: C, 72.13; H, 7.65. Found: C, 72.30; H, 7.80.

2i: ^1H NMR ($CDCl_3$, δ) 7.67 (d, J = 7.8 Hz, 1 H), 7.59 (t, J = 7.8 Hz, 1 H), 7.22 (d, J = 7.8 Hz, 1 H), 4.58 (s, 2 H), 3.95 (s, 3 H), 3.10 (br s, 1 H), 2.58 (t, J = 7.2 Hz, 2 H), 1.45−1.22 (m, 10 H), 0.82 (t, J = 6.6 Hz, 3 H); ^{13}C NMR ($CDCl_3$, d) 186.0, 185.1, 159.3, 146.1, 144.1, 134.8, 134.2, 119.5, 119.2, 117.4, 58.1, 56.3, 31.6, 29.9, 29.7, 28.9, 26.0, 22.5, 14.0;[1] IR (CH_2Cl_2, cm^{-1}) IR (CH_2Cl_2, cm^{-1}) 1656, 1588. Anal. Calcd for $C_{19}H_{24}O_4$: C, 72.13; H, 7.65. Found: C, 72.05; H, 7.77.

2j: ^1H NMR ($CDCl_3$, δ) 7.88 (d, J = 7.5 Hz, 1 H), 7.72 (s, 1 H), 7.44 (d, J = 7.5 Hz, 1 H), 6.80 (s, 1 H), 3.86 (t, J = 6.0 Hz, 2 H), 2.76 (t, J = 6.0 Hz, 2 H), 2.42 (s, 3 H); ^{13}C NMR ($CDCl_3$, δ) 185.3, 185.2, 148.4, 144.9, 136.2, 134.3, 131.8, 129.8, 126.7, 126.3, 60.7, 33.1, 21.7; IR (CH_2Cl_2, cm^{-1}) 1664, 1620, 1602. Anal. Calcd for $C_{13}H_{12}O_3$: C, 72.21; H, 5.59. Found: C, 72.47; H, 5.44.

2k: ^1H NMR ($CDCl_3$, δ) 8.04 (d, J = 8.4 Hz, 1 H), 7.49 (d, J = 2.4 Hz, 1 H), 7.19 (dd, J = 2.4 and 8.4 Hz, 1 H), 6.86 (s, 1 H), 3.94 (s, 3 H), 3.90 (m, 2 H), 2.82 (t, J = 5.7 Hz, 1 H); ^{13}C NMR ($CDCl_3$, δ) 185.0, 184.6, 164.0, 148.7, 136.1, 134.0, 129.1, 125.6, 120.3, 109.3, 61.0, 55.9, 33.3; IR (CH_2Cl_2, cm^{-1}) 1665, 1595.

2l: ^1H NMR ($CDCl_3$, δ) 7.88 (d, J = 7.8 Hz, 1 H), 7.72 (s, 1 H), 7.41 (d, J = 7.8 Hz, 1 H), 4.10−4.05 (m, 1 H), 3.91 (br s, 1 H), 2.74 (dd, J = 3.9 and 13.8 Hz, 1 H), 2.57 (dd, J = 8.1 and 13.8 Hz, 1 H), 2.42 (s, 3 H), 1.27 (d, J = 6.3, 3 H); ^{13}C NMR ($CDCl_3$, δ) 185.5 185.2, 148.2, 144.9, 136.7, 134.3, 131.8, 129.7, 126.7, 126.3, 66.7, 39.4, 23.5, 21.7; IR (CH_2Cl_2, cm^{-1}) 1664, 1602.

2m: ^1H NMR ($CDCl_3$, δ) 8.06−8.01 (m, 2 H), 7.70−7.66 (m, 2 H), 3.83 (t, J = 6.6 Hz, 2 H), 2.94 (t, J = 6.6 Hz, 2 H), 2.22 (s, 3 H); ^{13}C NMR ($CDCl_3$, δ) 185.4, 185.0, 145.1, 143.8, 133.5, 133.4, 132.1, 131.9, 126.3, 61.4, 30.6, 12.9; IR (CH_2Cl_2, cm^{-1}) 1666, 1624, 1596.

2n: ^1H NMR ($CDCl_3$, δ) 7.91 (d, J = 7.8 Hz, 1 H), 7.82 (s, 1 H), 7.46 (d, J = 7.8 Hz, 1 H), 3.82 (t, J = 6.6 Hz, 2 H), 2.92 (t, J = 6.6 Hz, 2 H), 2.57 (br s, 1 H), 2.46 (s, 3 H), 2.20 (s, 3 H); ^{13}C NMR ($CDCl_3$, δ) 185.4, 185.2, 144.9, 144.6, 143.7, 134.1, 131.9, 129.7, 126.6, 126.5, 61.5, 30.6, 21.8, 12.9; IR (CH_2Cl_2, cm^{-1}) 1661, 1618, 1602. Anal. Calcd for $C_{14}H_{14}O_3$: C, 73.03; H, 6.13. Found: C, 72.73; H, 6.22.

2o: ^1H NMR ($CDCl_3$, δ) 8.02 (d, J = 8.4 Hz, 1 H), 7.51 (d, J = 2.7 Hz, 1 H), 7.16 (dd, J = 2.7 and 8.4 Hz, 1 H), 3.94 (s, 3 H), 3.83 (t, J = 6.3 Hz, 2 H), 2.94 (t, J = 6.3 Hz, 2 H), 2.22 (s, 3 H); ^{13}C NMR ($CDCl_3$, δ) 185.1, 184.7, 163.9, 144.5, 143.9, 134.1, 128.9, 125.5, 120.1, 109.6, 61.6, 55.9, 30.6, 12.9; IR (CH_2Cl_2, cm^{-1}) 1661, 1596. Anal. Calcd for $C_{14}H_{14}O_4$: C, 68.28; H, 5.73. Found: C, 67.90; H, 5.47.

2p: ^1H NMR ($CDCl_3$, δ) 7.98 (d, J = 7.8 Hz, 1 H), 7.84 (s, 1 H), 7.51 (d, J = 7.8 Hz, 1 H), 6.79 (s, 1 H), 3.70 (t, J = 6.0 Hz, 2 H), 2.66 (t, J = 7.5 Hz, 2 H), 2.48 (s, 3 H), 1.84 (m, 2 H); ^{13}C NMR ($CDCl_3$, δ) 185.4, 185.3, 151.3, 144.9, 135.1, 134.4, 132.0, 130.0, 126.8, 126.4, 61.7, 31.3, 25.9, 21.8; IR (CH_2Cl_2, cm^{-1}) 1664, 1619, 1603.

2q: ^1H NMR ($CDCl_3$, δ) 7.98 (d, J = 8.7 Hz, 1 H), 7.42 (d, J = 2.7 Hz, 1 H), 7.13 (dd, J = 2.7 and 8.7 Hz, 1 H), 6.75 (s, 1 H), 3.91 (s, 3

(39) COLOC data for quinone **12** is reported in the supplementary material to ref 11.

(40) (a) Dötz, K. H.; Dietz, R.; Neugebauer, D. *Chem. Ber.* **1979**, *112*, 1486−1490. (b) Semmelhack, M. F.; Park, J. *Organometallics* **1986**, *5*, 2550−2552.

(41) (a) (Acylamino)carbene complexes of Cr have been reported to undergo preferential *E* insertion, whereas their Mo analogues afford products from (*Z*)-vinylcarbene intermediates: Grotjahn, D. B.; Kroll, F. E. K.; Schäfer, T.; Harms, K.; Dötz, K. H. *Organometallics* **1992**, *11*, 298−310. (b) Reactions of titanoxycarbene complexes such as $(CO)_5Cr{=}C(Ph)(OTiCp_2Cl)$ afford mixtures of quinone, cyclobutenone, and butenolide products, presumably arising from (*E*)- and (*Z*)-vinylketene isomers: Gross, M. F.; Finn, M. G., unpublished results.

H), 3.68 (t, J = 6.0 Hz, 2 H), 2.63 (J = 7.2 Hz, 2 H), 1.82 (m, 2 H); ^{13}C NMR ($CDCl_3$, δ) 185.0, 184.3, 163.9, 151.6, 134.7, 134.0., 129.0, 125.6, 120.1, 109.2, 61.6, 55.8, 31.1, 25.9; IR (CH_2Cl_2, cm^{-1}) 1663, 1595.

2r: ^{1}H NMR ($CDCl_3$, δ) 7.89 (d, J = 8.1 Hz, 1 H), 7.82 (s, 1 H), 7.47 (d, J = 8.1 Hz, 1 H), 4.65 (m, 1 H), 3.93 (d, J = 10.8 Hz, 1 H), 2.45 (s, 3 H), 2.15 (s, 3 H), 2.00−1.91 (m, 1 H), 1.78−1.69 (m, 1 H), 1.01 (t, J = 7.5 Hz, 3 H); ^{13}C NMR ($CDCl_3$, δ) 186.7, 185.2, 145.0, 143.1, 134.3, 131.5, 129.9, 126.7, 126.4, 72.8, 30.2, 21.8, 12.0, 10.6; IR ($CDCl_3$, cm^{-1}) 1662, 1647, 1601.

2s: ^{1}H NMR ($CDCl_3$, δ) 7.71 (d, J = 7.8 Hz, 1 H), 7.63 (t, J = 7.8, 1 H), 7.26 (d, J = 7.8 Hz, 1 H), 4.63 (dd, J = 2.7 and 8.7 Hz, 1 H), 3.99 (s, 3 H), 3.83 (br s, 1 H), 2.13 (s, 3 H), 2.04−1.94 (m, 1 H), 1.81−1.72 (m, 1 H), 1.01 (t, J = 7.5, 3 H); ^{13}C NMR ($CDCl_3$, δ) 186.5, 185.2, 159.6, 146.4, 141.2, 135.0, 133.9, 119.8, 119.2, 117.6, 73.1, 56.4, 30.2, 11.6, 10.6; IR ($CDCl_3$, cm^{-1}) 1647, 1621, 1588.

2t: ^{1}H NMR ($CDCl_3$, δ) 7.99 (d, J = 8.7 Hz, 1 H), 7.42 (d, J = 2.7 Hz, 1 H), 7.16 (dd, J = 2.7 and 8.7 Hz, 1 H), 6.83 (s, 1 H), 3.93 (t, J = 6.0, 2 H), 3.93 (s, 3 H), 2.82 (t, J = 6.0, 2 H); ^{13}C NMR ($CDCl_3$, δ) 185.1, 184.9, 164.2, 148.7, 136.3, 134.0, 129.2, 125.4, 120.4, 109.5, 61.1, 55.9, 33.3; IR (CH_2Cl_2, cm^{-1}) 1664, 1595.

2u: ^{1}H NMR ($CDCl_3$, δ) 7.63 (d, J = 7.8 Hz, 1 H), 7.54 (t, J = 7.8 Hz, 1 H), 7.17 (d, J = 7.8 Hz, 1 H), 3.91 (s, 3 H), 3.81 (t, J = 6.6 Hz, 2 H), 3.16 (br s, 1 H), 2.88 (t, J = 7.8 Hz, 2 H), 2.12 (s, 3 H); ^{13}C NMR ($CDCl_3$, δ) 184.8, 184.4, 158.9, 145.2, 142.5, 134.3, 133.8, 119.2, 118.7, 117.0, 61.1, 56.0, 30.8, 12.4; IR (CH_2Cl_2, cm^{-1}) 1658, 1628, 1588.

2v: ^{1}H NMR ($CDCl_3$, δ) 8.87 (d, J = 7.8 Hz, 1 H), 7.77 (s, 1 H), 7.42 (d, J = 7.8 Hz, 1 H), 3.60 (t, J = 6.0 Hz, 2 H), 2.69 (t, J = 7.5 Hz, 2 H), 2.42 (s, 3 H), 2.14 (s, 3 H), 1.72 (m, 2 H); ^{13}C NMR ($CDCl_3$, δ) 185.2, 185.0, 146.5, 144.4, 143.6, 134.0, 131.9, 129.6, 126.4, 61.4, 31.2, 22.9, 21.7, 12.5; IR (CH_2Cl_2, cm^{-1}) 1660, 1602. Anal. Calcd for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60. Found: C, 73.13; H, 6.46.

2w: ^{1}H NMR ($CDCl_3$, δ) 7.98 (d, J = 8.7 Hz, 1 H), 7.47 (d, J = 2.7 Hz, 1 H), 7.12 (dd, J = 2.7 and 8.7 Hz, 1 H), 3.91 (s, 3 H), 3.61 (t, J = 6.0 Hz, 2 H), 3.44 (br s, 1 H), 2.71 (t, J = 7.2 Hz, 2 H), 2.16 (s, 3 H), 1.75 (m, 2 H); ^{13}C NMR ($CDCl_3$, δ) 185.1, 184.4, 163.8, 146.7, 143.5, 134.0, 128.8, 125.5, 119.9, 109.5, 61.5, 55.8, 31.3, 22.8, 12.5; IR (CH_2Cl_2, cm^{-1}) 1661, 1595.

2x: ^{1}H NMR ($CDCl_3$, δ) 7.70 (d, J = 7.8 Hz, 1 H), 7.60 (t, J = 7.8 Hz, 1 H), 7.23 (d, J = 7.8 Hz, 1 H), 3.97 (s, 3 H), 3.62 (t, J = 6.0, 2 H), 2.70 (t, J = 7.5 Hz, 1 H), 2.13 (s, 3 H), 1.74 (m, 2 H); ^{13}C NMR ($CDCl_3$, δ) 185.2, 184.7, 159.4, 148.3, 141.5, 134.5, 134.3, 119.8, 119.0, 117.3, 61.7, 56.3, 31.4, 23.2, 12.3; IR (CH_2Cl_2, cm^{-1}) 1656, 1588. Anal. Calcd for $C_{15}H_{16}O_4$: C, 69.22; H, 6.20. Found: C, 68.79; H, 6.30.

3c: ^{1}H NMR ($CDCl_3$, δ) 7.61 (d, J = 7.8 Hz, 1 H), 7.29 (s, 1 H), 7.18 (d, J = 7.8 Hz, 1 H), 4.06 (dd, J = 5.1 and 11.1 Hz, 1 H), 3.89 (dd, J = 6.9 Hz and 11.1 Hz, 1 H), 3.14 (m, 1 H), 2.45 (s, 3 H), 2.42 (m, 1 H), 1.45 (d, J = 6.9 Hz, 3 H); ^{13}C NMR ($CDCl_3$, δ) 207.8, 159.2, 146.6, 133.6, 128.9, 125.5, 123.4, 61.8, 58.1, 35.9, 22.2, 19.4; IR ($CDCl_3$, cm^{-1}) 1705, 1609.

3m: ^{1}H NMR ($CDCl_3$, δ) 7.74 (d, J = 7.5 Hz, 1 H), 7.64 (t, J = 7.5 Hz, 1 H), 7.50 (d, J = 7.5 Hz, 1 H), 7.39 (t, J = 7.5 Hz, 1 H), 3.97−3.81 (m, 2 H), 3.14−3.05 (m, 1 H), 2.42−2.36 (m, 1 H), 2.07−1.91 (m, 2 H), 1.48 (d, J = 7.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$, δ) 208.0, 158.1, 135.5, 135.2, 127.4, 124.9, 123.8, 61.8, 55.4, 40.2, 32.8, 19.4; IR (CH_2Cl_2, cm^{-1}) 1707, 1605.

3n: ^{1}H NMR ($CDCl_3$, δ) 7.62 (d, J = 7.8 Hz, 1 H), 7.27 (s, 1 H), 7.20 (d, J = 7.8 Hz, 1 H), 3.97−3.80 (m, 2 H), 3.03 (dt, J = 2.1 and 6.9 Hz, 1 H), 2.46 (s, 3 H), 2.40−2.33 (m, 1 H), 2.02−1.92 (m, 2 H), 1.45 (d, J = 6.9 Hz, 3 H); ^{13}C NMR ($CDCl_3$, δ) 208.8, 158.7, 146.7, 133.2, 128.9, 125.2, 123.7, 62.0, 55.9, 40.1, 32.7, 22.2, 19.3; IR (CH_2Cl_2, cm^{-1}) 1706, 1609.

3o: ^{1}H NMR ($CDCl_3$, δ) 7.67 (d, J = 8.4 Hz, 1 H), 6.93−6.89 (m, 2 H), 3.97−3.79 (m, 2 H), 3.90 (s, 3 H), 3.03−2.99 (m, 1 H), 2.40−2.34 (m, 1 H), 2.00−1.92 (m, 2 H), 1.45 (d, J = 6.9 Hz, 3 H); ^{13}C NMR ($CDCl_3$, δ) 207.3, 165.9, 161.2, 128.7, 125.7, 115.4, 108.3, 62.0, 55.9, 55.7, 40.3, 32.9, 19.3; IR (CH_2Cl_2, cm^{-1}) 1699, 1666, 1599.

Nitrates produced by prolonged exposure to the workup conditions have similar spectroscopic properties to the alcohols described above, except for a characteristic ≈1 ppm downfield shift in the ^{1}H NMR resonances of the carbinol protons.

4c: ^{1}H NMR ($CDCl_3$, δ) 7.74 (d, J = 7.8 Hz, 1 H), 7.30 (s, 1 H), 7.21 (d, J = 7.8 Hz, 1 H), 6.32 (d, J = 2.1 Hz, 1 H), 5.56 (d, J = 2.1 Hz, 1 H), 3.81 (q, J = 7.2 Hz, 1 H), 2.46 (s, 3 H), 1.46 (d, J = 7.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$, δ) 193.7, 155.7, 150.2, 146.4, 135.3, 129.0, 125.4, 124.2, 118.1, 36.9, 22.3, 20.1; IR (CH_2Cl_2, cm^{-1}) 1702, 1669, 1643, 1610.

4r: ^{1}H NMR ($CDCl_3$, δ) 7.72 (d, J = 7.8 Hz, 1 H), 7.28 (s, 1 H), 7.19 (d, J = 7.8 Hz, 1 H), 6.77 (dt, J = 1.8 and 7.8 Hz, 1 H), 3.87 (q, J = 7.2 Hz, 1 H), 2.45 (s, 3 H), 2.41−2.31 (m, 2 H), 1.42 (d, J = 7.2 Hz, 3 H), 1.15 (t, J = 7.5 Hz, 3 H); ^{13}C NMR ($CDCl_3$, δ) 193.3, 156.0, 145.8, 141.4, 139.2, 135.1, 128.8, 125.4, 124.0, 35.8, 22.6, 22.3, 20.8, 12.3; IR ($CDCl_3$, cm^{-1}) 1697, 1648, 1611.

4s: ^{1}H NMR ($CDCl_3$, δ) 7.54 (t, J = 7.8 Hz, 1 H), 7.03 (d, J = 7.8 Hz, 1 H), 6.81 (d, J = 7.8 Hz, 1 H), 6.72 (dt, J = 1.8 and 7.8 Hz, 1 H), 3.96 (s, 3 H), 3.85 (q, J = 7.2 Hz, 1 H), 2.41−2.29 (m, 2 H), 1.41 (d, J = 7.2 Hz, 3 H), 1.14 (t, J = 7.5 Hz, 3 H).

5j: ^{1}H NMR ($CDCl_3$, δ) 7.62 (d, J = 8.7 Hz, 1 H), 7.58 (s, 1 H), 7.34 (d, J = 8.7 Hz, 1 H), 7.16 (s, 1 H), 4.30 (t, J = 7.2 Hz, 2 H), 2.96 (t, J = 7.2 Hz, 2 H), 2.48 (s, 3 H), 2.47 (s, 3 H), 2.42 (s, 3 H), 2.03 (s, 3 H); ^{13}C NMR ($CDCl_3$, δ) 170.7, 169.1, 143.7, 142.5, 136.3, 129.3, 126.7, 126.0, 124.8, 121.3, 120.2, 119.6, 63.1, 29.6, 21.6, 20.7, 20.3; IR (CH_2Cl_2, cm^{-1}) 1763, 1738, 1614. Anal. Calcd for $C_{19}H_{20}O_6$: C, 66.27; H, 5.85. Found: C, 66.50; H, 5.68.

5n: ^{1}H NMR ($CDCl_3$, δ) 7.56 (d, J = 8.4 Hz, 1 H), 7.46 (s, 1 H), 7.30 (d, J = 8.4 Hz, 1 H), 4.22 (t, J = 7.5 Hz, 2 H), 3.04 (m, 2 H), 2.52 (s, 3 H), 2.49 (s, 6 H), 2.32 (s, 3 H), 2.06 (s, 3 H); ^{13}C NMR ($CDCl_3$, δ) 171.0, 169.6, 169.0, 143.4, 142.2, 136.6, 128.6, 126.8, 126.5, 124.8, 124.2, 121.3, 120.0, 62.7, 27.1, 21.8, 20.9, 20.6, 20.5, 13.0; IR (CH_2Cl_2, cm^{-1}) 1756, 1739, 1610.

6j: ^{1}H NMR ($CDCl_3$, δ) 7.63 (d, J = 7.8 Hz, 1 H), 7.24 (s, 1 H), 7.12 (d, J = 7.8 Hz, 1 H), 4.24 (t, J = 6.6 Hz, 2 H), 3.30 (dd, J = 7.8 and 17.1 Hz, 1 H), 2.94−2.69 (m, 2 H), 2.42 (s, 3 H), 2.36−2.26 (m, 1 H), 2.20 (s, 3 H), 1.82−1.72 (m, 1 H); ^{13}C NMR ($CDCl_3$, δ) 207.2, 170.9, 153.8, 146.0, 134.0, 128.7, 126.8, 123.7, 62.6, 44.5, 32.5, 30.3, 22.0, 20.9; IR (CH_2Cl_2, cm^{-1}) 1735, 1707, 1611.

6n: ^{1}H NMR ($CDCl_3$, δ) 7.62 (d, J = 7.8 Hz, 1 H), 7.27 (s, 1 H), 7.19 (dd, J = 0.9 and 7.8 Hz, 1 H), 4.28 (t, J = 6.6 Hz, 2 H), 3.09−3.05 (m, 1 H), 2.45 (s, 3 H), 2.31−2.22 (m, 2 H), 2.03 (s, 3 H), 1.91−1.82 (m, 1 H), 1.43 (d, J = 6.9 Hz, 3 H); ^{13}C NMR ($CDCl_3$, δ) 206.7, 171.0, 158.5, 146.2, 133.4, 128.9, 125.4, 123.5, 62.6, 53.3, 39.3, 29.6, 22.2, 20.9, 20.4; IR (CH_2Cl_2, cm1−^{1}) 1732, 1710, 1609.

7 (from *p*-MePh carbene complexes and 1-hexyne): ^{1}H NMR ($CDCl_3$, δ) 7.88 (d, J = 7.8 Hz, 1 H), 7.82 (s, 1 H), 7.46 (d, J = 7.8 Hz, 1 H), 6.69 (s, 1 H), 2.53 (t, J = 7.2 Hz, 2 H), 2.44 (s, 3 H), 1.57−1.47 (m, 2 H), 1.42−1.34 (m, 2 H), 0.92 (t, J = 7.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$, δ) 185.4, 184.9, 151.5, 147.8, 144.5, 134.6, 134.1, 128.7, 126.8, 126.0, 30.0, 29.1, 22.4, 21.7, 13.7; IR (CH_2Cl_2, cm^{-1}) 1663, 1602.

7 (from *p*-MePh carbene complexes and 3-hexyne): ^{1}H NMR ($CDCl_3$, δ) 7.86 (δ, J = 7.8 Hz, 1 H), 7.76 (s, 1 H), 7.39 (d, J = 7.8 Hz, 1 H), 2.57 (q, J = 7.5 hz, 4 H), 2.40 (s, 3 H), 1.09 (t, J = 7.5 Hz, 6 H); ^{13}C NMR ($CDCl_3$, δ) 185.1, 184.7, 147.8, 147.6, 144.1, 133.8, 132.0, 129.9, 126.3, 126.2, 21.6, 20.0, 13.9; IR (CH_2Cl_2, cm^{-1}) 1657, 1602.

7 (from *p*-OMePh carbene complex and 3-hexyne): ^{1}H NMR ($CDCl_3$, δ) 8.01 (d, J = 8.7 Hz, 1 H), 7.51 (d, J = 2.7 Hz, 1 H), 7.15 (dd, J = 8.7 Hz, 1 H), 3.93 (s, 3 H), 2.63 (q, J = 7.5 Hz, 4 H), 1.14 (t, J = 7.5 Hz, 6 H).

9: ^{1}H NMR ($CDCl_3$, δ) 7.64 (d, J = 1.5 Hz, 1 H), 6.80 (d, J = 1.5 Hz, 1 H), 4.50 (br s, 1 H), 3.80 (t, J = 6.6 Hz, 2 H), 2.87 (t, J = 6.6 Hz, 2 H), 2.13 (s, 3 H); ^{13}C NMR ($CDCl_3$, δ) 182.7, 176.1, 150.9, 147.9, 143.1, 140.3, 128.2, 108.1, 61.3, 29.6, 12.5; IR (CH_2Cl_2, cm^{-1}) 1665. Anal. Calcd for $C_{11}H_{10}O_4$: C, 64.08; H, 4.89. Found: C, 63.33; H, 5.14.

11: ^{1}H NMR ($CDCl_3$, δ) 6.54 (t, J = 1.5 Hz, 1 H), 3.71 (t, J = 6.6 Hz, 2 H), 2.92 (br s, 1 H), 2.76 (t, J = 6.6 Hz, 2 H), 2.03 (s, 3 H), 2.00 (d, J = 1.5 Hz, 3 H); ^{13}C NMR ($CDCl_3$, δ) 188.2, 187.5, 145.3, 142.4, 141.2, 133.2, 61.2, 30.1, 15.8, 12.0; IR (CH_2Cl_2, cm^{-1}) 1649, 1617.

12: ^{1}H NMR ($CDCl_3$, δ) 7.90 (d, J = 7.8 Hz, 1 H), 7.84 (s, 1 H), 7.49 (d, J = 7.8 Hz, 1 H), 6.84 (d, J = 0.9 Hz, 1 H), 3.88 (t, J = 6.0 Hz, 2 H), 2.80 (dt, J = 6.0, 0.9 Hz, 2 H), 2.41 (s, 3 H); ^{13}C NMR

($CDCl_3$, δ) 185.9, 184.8, 148.2, 144.8, 136.5, 134.5, 132.0, 129.8, 127.0, 126.3, 61.0, 33.2, 21.8; IR (CH_2Cl_2, cm^{-1}) 1663, 1619 w, 1603 s.

Mixture of 14 and 15: **14** and **15** display identical ^1H NMR and IR spectra in $CDCl_3$; asterisks mark the resolved ^{13}C resonances of the minor component (**15**, identical to the methyl ether of **2n**). ^1H NMR ($CDCl_3$, δ) 7.95 (d, J = 7.8 Hz, 1 H), 7.85 (s, 1 H), 7.47 (d, J = 7.8 Hz, 1 H), 3.53 (t, J = 6.9 Hz, 2 H), 3.32 (s, 3 H), 2.93 (t, J = 6.9 Hz, 2 H), 2.47 (s, 3 H), 2.21 (s, 3 H); ^{13}C NMR ($CDCl_3$, δ) 184.9*, 184.5 (coincident carbonyl resonances of **14**), 184.1*, 144.7, 144.5*, 144.0, 143.4*, 143.2, 133.8, 131.8*, 131.7, 129.6, 129.5*, 126.3, 126.1, 70.7, 58.4, 27.4, 21.5, 12.6; IR ($CDCl_3$, cm^{-1}) 1658, 1619, 1603.

17: ^1H NMR ($CDCl_3$, δ) 8.11 (d, J = 8.4 Hz, 1 H), 7.50 (s, 1 H), 7.33 (d, J = 8.4 Hz, 1 H), 7.01 (s, 1 H), 4.14 (m, 2 H), 2.92 (m, 2 H), 2.51 (s, 3 H), 2.45 (s, 3 H), 2.05 (m, 2 H), 1.78 (m, 2 H); ^{13}C NMR ($CDCl_3$, δ) 169.8, 153.4, 140.9, 135.6, 128.8, 128.3, 127.0, 126.2, 122.3, 120.7, 119.6, 73.2, 34.1, 32.4, 25.6, 21.8, 20.9; IR (CH_2Cl_2, cm^{-1}) 1761, 1611.

21: ^1H NMR ($CDCl_3$, δ) 7.70 (d, J = 7.8 Hz, 1 H), 7.63 (t, J = 7.8 Hz, 1 H), 7.26 (d, J = 7.8 Hz, 1 H), 5.87–5.73 (m, 1 H), 5.12–5.05 (m, 2 H), 4.73–4.65 (m, 3 H), 4.00 (s, 3 H), 3.72 (d, J = 11.1 Hz, 1 H), 3.44–3.30 (t superimposed on m, 2 H), 2.00 (apparent q, J = 9.0 Hz, 1 H), 1.67–1.56 (m, 2 H), 1.45–1.34 (m, 1 H), 0.93 (t, J = 7.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$, δ) 186.7, 184.6, 159.6, 147.6, 141.4, 135.0, 133.8, 133.5, 119.9, 119.2, 117.6, 117.0, 71.1, 56.4, 39.3, 29.6, 19.4, 13.8; IR (CH_2Cl_2, cm^{-1}) 1659, 1647, 1617, 1588. Anal. Calcd for $C_{18}H_{20}O_4$: C, 71.98; H, 6.71. Found: C, 71.66; H, 7.03.

22: ^1H NMR ($CDCl_3$, δ) 7.52 (t, J = 7.8 Hz, 1 H), 7.05 (d, J = 7.8 Hz, 1 H), 6.81 (d, J = 7.8 Hz, 1 H), 6.76 (t, J = 7.8 Hz, 1 H), 5.57–5.43 (m, 1 H), 4.99–4.87 (m, 2 H), 3.95 (s, 4 H, OMe superimposed on methine resonance), 2.73–2.52 (m, 2 H), 2.38–2.24 (m, 2 H), 1.61–1.51 (m, 2 H), 0.98 (t, J = 7.5 Hz, 3 H); ^{13}C NMR ($CDCl_3$, δ) 191.4, 158.4, 155.6, 139.8, 136.9, 135.9, 135.5, 133.8, 117.8, 17.3, 109.3, 55.7, 40.5, 38.7, 31.4, 22.0, 14.0; IR (CH_2Cl_2, cm^{-1}) 1699, 1651, 1591.

Acknowledgment. We thank the National Science Foundation (CHE 91-09000), the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Mobil Corporation (fellowship award to M.F.G.) for support of this work. We are very grateful to Dr. Michal Sabat for X-ray crystallography, to Dr. Laurie Kelsh for COLOC NMR measurements, and to Ms. Bonnie Balzer for assistance in the regiochemical characterization of compound **12**.

Supplementary Material Available: Details of regioisomer assignments by NMR and X-ray crystallography (17 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.