Journal of Organometallic Chemistry, 334 (1987) 9–56
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Solvent, chelation and concentration effects on the benzannulation reaction of chromium carbene complexes and acetylenes

Kin Shing Chan, Glen A. Peterson, Timothy A. Brandvold, Katherine L. Faron *, Cynthia A. Challener *, Carol Hyldahl and William D. Wulff **,*

Searle Chemistry Laboratory, Department of Chemistry, The University of Chicago, Chicago, Illinois 60637 (U.S.A.)

(Received February 5th, 1987)

Abstract

The reactions of a number of chromium carbene complexes $(CO)_5Cr{=}C(OMe)R$ (R = Ph, *o*-OMePh, *p*-OMePh, *o*-O-tBuPh, 1-C_6H_9, 1-C_5H_7O) were examined with a variety of acetylenes ($R'CCR^2$, R^1, R^2 = H, Me, Et, n-Pr, Ph, $SiMe_3$) in solvents ranging from low to high coordinating ability. The high selectivity for the benzannulated product from the reactions of simple α,β-unsaturated complexes is not affected by changes in solvent or substituents on the acetylene. The reactions of aryl complexes with acetylenes are quite sensitive to the nature of the solvent and the acetylene. The highest selectivities and efficiencies for the benzannulated product from the reactions of aryl complexes are with solvents of low coordinating ability. Solvents with intermediate coordinating ability and small size give high selectivity for cyclobutenone formation for reactions with disubstituted acetylenes. Solvents with high coordinating ability give the least selective reactions and a considerable amount of indene products. An *o*-methoxy group on the aryl substituent of the carbene complex can chelate to the metal center during the course of the benzannulation reaction and, in acetonitrile, alter the product distribution in favor of the cyclobutenone product. An amino substituted complex, $(CO)_5Cr{=}C(NMe_2)Ph$, was found to react with diethylacetylene in THF to give indene products. The reactions of aryl complexes with alkynes can be accelerated by ultraviolet irradiation which results in high selectivity for the benzannulated product at as low a temperature as $-78\,^\circ C$, and high selectivity for indene products for those complexes having a chelating group (methoxy) on the aryl ring. Finally, the product distribution from the reaction of the *o*-methoxyphenyl complex with diethylacetylene was found to be dependent on alkyne concentration, a phenomenon not previously observed for the reactions of carbene complexes and acetylenes.

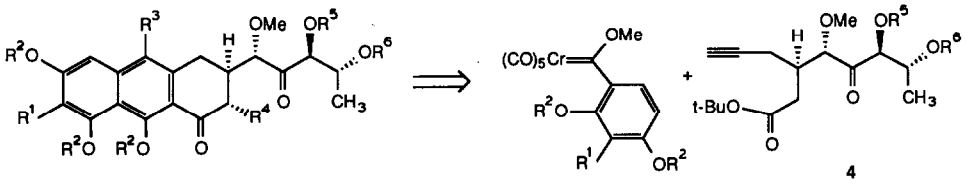
---

* National Institute of Health Predoctoral Fellow.
** Eli Lilly Young Scholar 1986–1987.

0022-328X/87/$03.50

Introduction

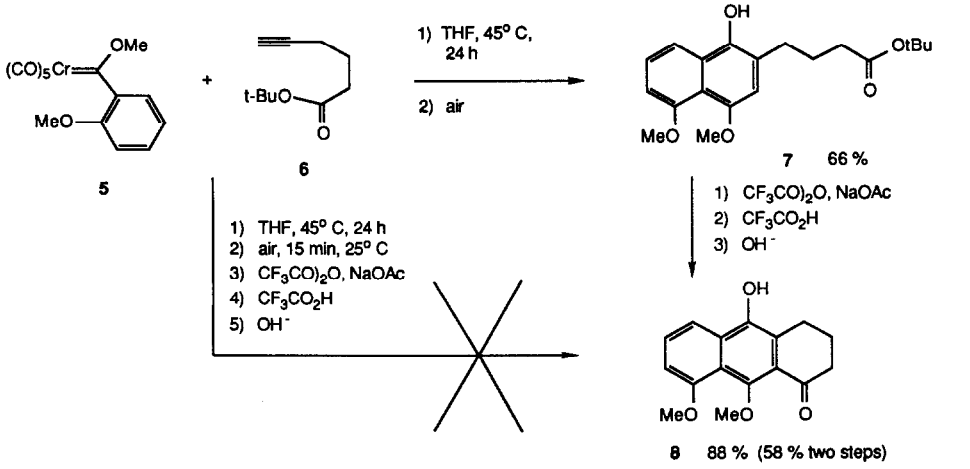
The reaction of Fischer carbene complexes of chromium with acetylenes was first reported twelve years ago and was observed to give a product containing a new benzene nucleus [1]. This benzannulation reaction has in the last few years been utilized in a number of organic syntheses and new applications will undoubtedly continue to appear in the literature [2,3*]. A number of the aspects of this reaction has been explored, including the regiochemistry of the alkyne incorporation [4], however, very little is known about the effects of solvent on this reaction [3b*,5,6,7]. Our interest in the effects of solvent on this reaction began in response to problems that arose in the utilization of the benzannulation reaction in a one-pot tandem sequence with Friedel–Crafts acylations as part of several total syntheses and is illustrated retro-synthetically for an approach to the synthesis of the anti-tumor antibiotic olivin 1 [8*], which involves the proposed one-pot synthesis of **2** from the carbene complex **3** and the acetylene **4**.



1 R^1, R^2, R^3, R^5, R^6 = H R^4 = OH

2 R^1, R^4 = H; R^2 = Me; R^3 = OH; R^5, R^6 = $C(CH_3)_2$

As a model study for this tandem benzannulation/Friedel–Crafts sequence, we investigated the reaction of the *o*-methoxyphenyl carbene complex **5** and the acetylene **6** [2a,3b*]. The benzannulation and Friedel–Crafts reaction separately were uneventful as the naphthol **7** and the tricyclic ketone **8** were obtained in 66 and 88% yields, respectively. The benzannulation reactions were normally carried out in ethereal solvents and thus the reaction of **5** and **6** was run in THF, and the

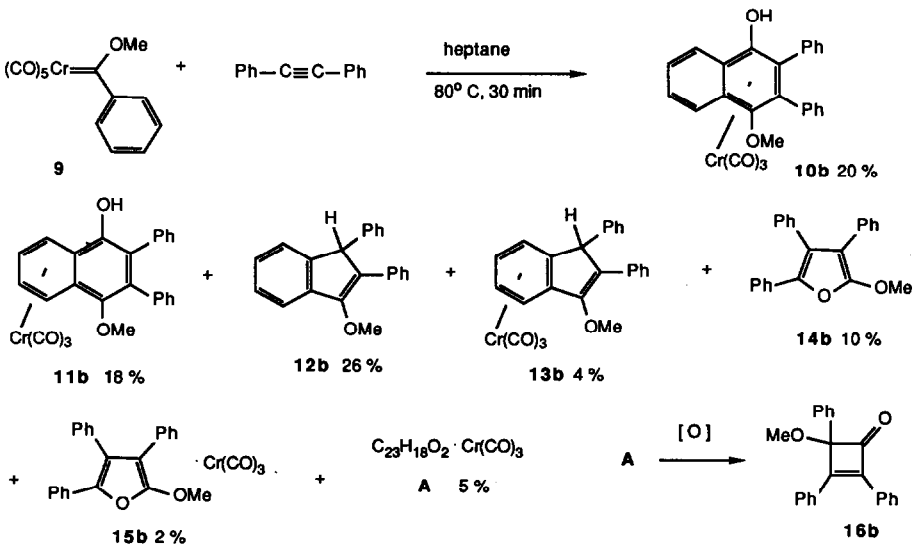


* This and other references marked with asterisks indicate notes occurring in the list of references.

intramolecular Friedel–Crafts cyclization of **7** was performed in trifluoroacetic anhydride. When both steps were attempted sequentially in a single-pot with THF as solvent a large number of products were observed with very little of the desired cyclized product. Apparently, the Friedel–Crafts reaction was incompatible with THF as solvent, and thus a solvent was needed that was compatible with both reactions. We herein describe the results of an extensive investigation on the effects of solvent on the benzannulation reaction of chromium carbene complexes with acetylenes which may prove to be of value in further applications of this synthetically powerful reaction.

Results and discussion

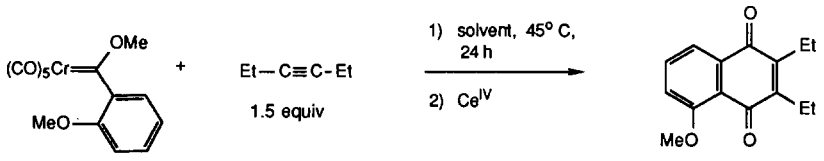
At the time we began this work there was only one report in the literature of a reaction of a chromium carbene complex with an acetylene in a non-ethereal solvent [5]. The reaction of the phenylcarbene complex **9** with diphenylacetylene in heptane was reported to give the seven products indicated in Scheme 1. The same reaction in n-butyl ether had been earlier reported to give exclusively the naphthol complex **10** [1]. Although this observation was discouraging from the synthetic point of view, it was nonetheless one of great significance because it revealed for the first time the complexity of these reactions and their sensitivity to reaction conditions and that these factors must be taken into consideration at the outset of any synthetic endeavor. The major organic structural types isolated were naphthalenes, indenes and furans. A very recent report in the literature has appeared which describes an unsuccessful attempt to optimize indene formation from the reaction of a chromium carbene complex with various alkynes in alkane solvents for the purpose of synthetic entry into aromatic C-ring steroids [6]. The reaction of complex **9** and diphenylacetylene also gave a small amount of an unidentified organometallic compound (**A**) which gave the cyclobutenone **16** as the major product upon



Scheme 1

oxidation. Perhaps as a consequence of the reaction outlined in Scheme 1, it is stated in most major reviews that coordinating solvents are necessary for the selective formation of the naphthol products [3a,c*].

The first benzannulation reaction that we examined with respect to solvent variation was a surprise. The annulation of the *o*-methoxyphenylcarbene complex **5** had been previously investigated in the course of its application to anthracycline synthesis but only in THF as solvent [4c]. On the basis of the observation of the reaction of the phenyl complex **9** and diphenylacetylene in heptane (Scheme 1), it was unexpected to find that the reaction of complex **5** with diethylacetylene in hexane gave the naphthoquinone **17a** (after ceric ammonium nitrate oxidation) in

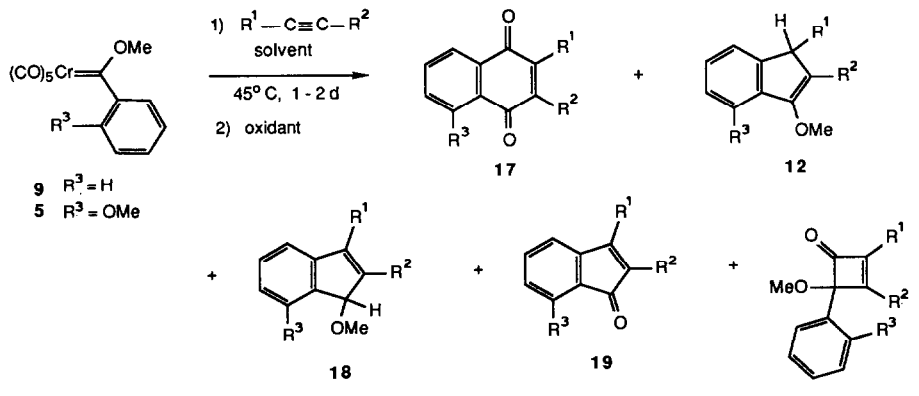


5
0.15-0.20 M

17a
THF 55-65 %
hexane 83 %

higher yield than the corresponding reaction in THF. The results of the examination of the reaction of the *o*-methoxyphenylcarbene complex **5** with diethylacetylene in a variety of solvents are presented in Table 1 and the range of products is indicated in Scheme 2. The best results are obtained in the most non-coordinating solvents, intermediate results are obtained with solvents of intermediate coordinating ability, and the worst results, in terms of product selectivity were obtained from solvents of high coordinating ability or with solvents of intermediate coordinating ability with small size (acetonitrile).

It should be pointed out that in none of the studies reported here were attempts made to isolate furan products. For example, in most of the reactions in Table 1 an oxidative workup with either Ce^{IV} or Fe^{III} was employed which are conditions that can destroy furan products. However, even for those reactions where an oxidative workup with air was used the furan products (with the exception of the triphenyl-



9 R^3 = H
5 R^3 = OMe

17 **12** **18** **19** **16**

Scheme 2

Table 1

Reaction of complex **5** with diethylacetylene [a]

R^1	R^2	R^3	solvent	donor number[b]	dielectric constant[b]	oxidant	isolated yields (%) 17a	12a	18a	19a	16a	20a
Et	Et	OMe	hexane[c]	0.0	1.9	Ce^{IV}	83					
			benzene[c]	0.1	2.3	Ce^{IV}	77					
			THF	20	7.6	Ce^{IV}	55-65[j]		18-26[j]	4	≤3	
			THF			air	_[g]	≤3	25			
			DMTHF[c,d]			Ce^{IV}	69					
			dioxane[c]	14.8	2.2	Ce^{IV}	70					
			CH_2Cl_2[c]		9.1	Ce^{IV}	65					
			CH_3NO_2[c]	2.7	35.9	Ce^{IV}	60					
			CH_3OH[e]	19.0	32.7	Fe^{III}	51		20			
			CH_3CN	14.1	38.0	air	<2	5	12		43	
			CH_3CN/CO[f]			air		_[g]	12		36	
			DMF	26.6	36.1	air/S_8	_[g]		19		28	
			DMF			Ce^{IV}	12[h]			<15[i]		16
			HMPA	38.8	30.0	Ce^{IV}	12	15	6		29	

[a] All reactions were carried out at 0.15–0.20 *M* in **5** with 1.5 equiv. of diethylacetylene at 45°C with a second 1.5 equiv. of acetylene added toward the end of the reaction (after 24 h). [b] Reference 9. [c] Reactions screened only for the quinone **17a**. [d] 2,5-Dimethyltetrahydrofuran. [e] Two minor products were isolated (< 5% each) but were not characterized. [f] Reaction carried out under 1 atm of carbon monoxide. [g] Isolation not attempted. [h] HPLC yield. [i] Isolated by preparative GC but not quantified. [j] See Table 4.

furan **14b**) may not have been isolable since it is our experience that in most cases the silica gel needs to be pretreated with triethylamine and the chromatography solvents degassed before the furans will survive isolation by silica gel chromatography [13]. In addition, the amounts of indenes and cyclobutenones were determined only for selected reactions, and many of the reactions in Tables 1–6 were screened only for the quinone product and these are so indicated in each Table.

The reactions in solvents with poor coordinating ability were highly selective for naphthoquinone formation. The reactions in hexane and benzene were very clean and gave the highest yields of the naphthoquinone **17a**. Ethereal solvents with intermediate coordinating ability also were selective for quinone formation. The naphthoquinone **17a** is the major product obtained from the reaction in methanol after the crude reaction mixture is oxidized with ferric chloride-DMF complex [10], however a substantial amount of the indene **18a** was also isolated from this reaction. Two other compounds were isolated from the reaction in methanol in small amounts (< 5% each) that were not characterized, but could have been ketene trapping products [11]. After, the reaction of complex **5** and diethylacetylene in

Table 2
Reactions of complexes **5** and **9** with various acetylenes [a]

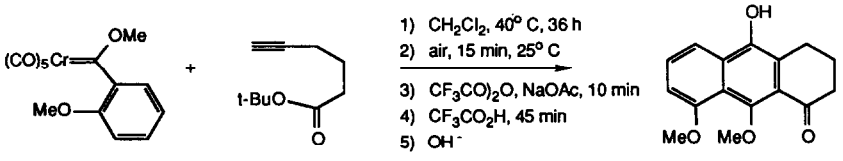
entry	series	R^1	R^2	R^3	solvent	isolated yields (%)				
						17	**12**	**18**	**19**	**16**
1	b	Ph	Ph	H	THF[b]	59				
2		Ph	Ph	H	hexane[c,d]	41			38	
3		Ph	Ph	H	CH_3CN		4	15		51
4		Ph	Ph	H	benzene	36				21
5		Ph	Ph	H	DMF		83[e]			
6	c	Et	Et	H	THF	88	≤0.3[t]	≤0.3[t]		
7		Et	Et	H	hexane	84[f]				
8		Et	Et	H	CH_3CN[n]	38	8	5		23
9	d	n-Pr	H	H	THF[q]	73				
10		n-Pr	H	H	hexanes	80[g]				
11		n-Pr	H	H	CH_3CN[s]	53[p]				
12	e	Ph	H	H	THF[q]	87				
13		Ph	H	H	hexane[q]	57[h]				
14	f	t-Bu	CH_3	H	THF[n]	26[i]				14
15		t-Bu	CH_3	H	hexane	32	(-)[r]	(-)[r]		23[n]
16		t-Bu	CH_3	H	CH_3CN					27
17	a	Et	Et	OMe	THF	55-65[u]		18-26[u]	4	≤3
18		Et	Et	OMe	hexanes[q]	83				
19		Et	Et	OMe	CH_3CN[o]	<2[j]	5	12		43
20	g	Me	Me	OMe	THF[q]	68				
21		Me	Me	OMe	CH_3CN[o]	3	9	11		30
22	h	n-Pr	H	OMe	THF[q]	74				
23		n-Pr	H	OMe	CH_3CN[s]	57-69[p]				
24		n-Pr	H	OMe	hexane[q]	88				
25		n-Pr	H	OMe	benzene[q]	90				
26		n-Pr	H	OMe	CH_2Cl_2[q]	71				
27	i	i-Pr	CH_3	OMe	THF[q]	61[k,l]				
28	j	n-Pr	CH_3	OMe	THF[q]	64[k,m]				

Table 2, footnotes

[a] Oxidative workup with cerium(IV) ammonium nitrate was employed in all reactions unless otherwise specified; all reactions were run at 0.1–0.2 *M* in **5** or **9** with 1.5 equiv. of alkyne followed by an additional 1.5 equiv. of alkyne near the end of the reaction (after 24 h). [b] Reference 1. [c] No attempt was made to isolate the furan **14** or the cyclobutenone **16** from this reaction. [d] Reference 5. [e] Reference 7. [f] Biphenyl was also produced from this reaction in 14% yield. [g] 12% yield of an unidentified product was also obtained. [h] Less than 15% of each of three minor products were also formed. [i] Only the naphthol complex **2f** has been reported previously, reference 4b. [j] Reference 3b. [k] Reference 4c. [l] 4.8/1.0 mixture of isomers. [m] 2.9/1.0 mixture of isomers. [n] Oxidative workup with ferric chloride-DMF complex. [o] Air oxidation. [p] See Scheme 10. [q] Reactions screened only for quinone **17**. [r] A fraction was obtained (11%) that was tentatively identified as a mixture of indenes.[s] Reaction screened for quinone **17** and cyclobutenone **16**. [t] Determined by capillary GC with diphenylacetylene as internal standard. [u] See Table 4.

acetonitrile had gone to completion, the crude mixture was oxidized by exposure to air and the major product was isolated and identified as the cyclobutenone **16a** in 43% yield, which was formed along with a small amount of the indenes **18a** (12%) and **12a** (5%). This was the first time that a cyclobutenone was isolated as the major product from the reaction of a chromium carbene complex and an acetylene except where the annulation reaction was blocked [4a,12]. An aliquot of the crude mixture from the acetonitrile reaction was oxidized with ceric ammonium nitrate and none of the quinone **17a** could be detected. Acetonitrile is a solvent with intermediate coordinating ability and small size and is observed to give the highest selectivity for cyclobutenone formation. The solvents with the highest coordinating ability (DMF and HMPA) in Table 1 gave the least selective product distributions with substantial amounts of indenes and cyclobutenones being formed along with small amounts of naphthoquinone [3b*].

This study did result in the resolution of the difficulties encountered in the one-pot benzannulation/Friedel–Crafts sequence for the synthesis of olivin. A number of the solvents in Table 1 that are selective for naphthoquinone formation should also be compatible with intramolecular Friedel–Crafts acylations. When the one-pot double-cyclization sequence was carried out with carbene complex **5** and the alkyne **6** in methylene chloride solvent the desired tricyclic ketone **8** was obtained in 64% yield [3b*]. From the data to be discussed later in Table 2, it appears that even higher yields for the benzannulation/Friedel–Crafts sequence may be possible with hexane or benzene as solvent (entries 24 and 25).



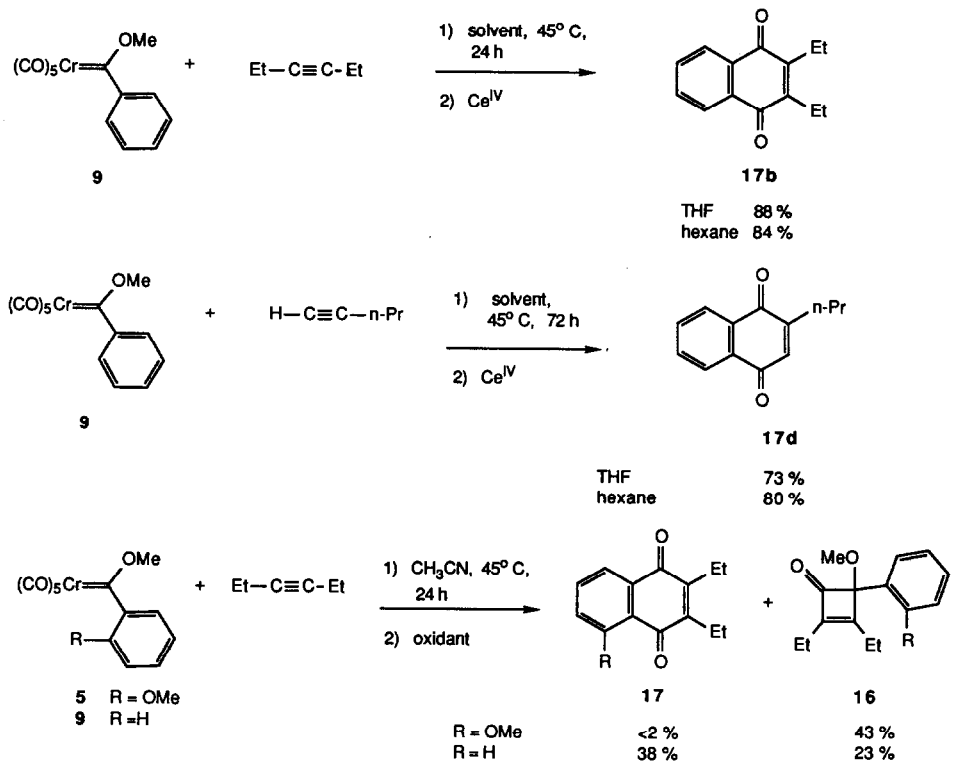
5 **6** **8** 64 %

The study of the effect of solvent on the reaction of the *o*-methoxyphenylcarbene complex **5** with diethylacetylene also raises the central issue as to whether the optimum solvent for the benzannulation reaction is one with low coordinating ability such as an alkane which is suggested by the data for the *o*-methoxyphenyl complex presented in Table 1, or an ethereal solvent with moderate coordinating ability as suggested by the reaction of the phenyl complex **9** with diphenylacetylene

which in heptane gives rise to the complex mixture indicated in Scheme 1, and in n-butyl ether gives exclusively the benzannulated product **10**. Specifically, is the difference between these observations due to the difference between diethylacetylene and diphenylacetylene, or due to the presence or absence of the *o*-methoxy group on the phenyl ring of the carbene complex? The data presented in Table 2 are the results of an extensive comparative study of the reactions of both the *o*-methoxyphenyl complex **5** and the phenyl complex **9** with a variety of acetylenes in a number of different solvents, from which it is clear that the differences in the two observations above have to do with the differences between diethylacetylene and diphenylacetylene.

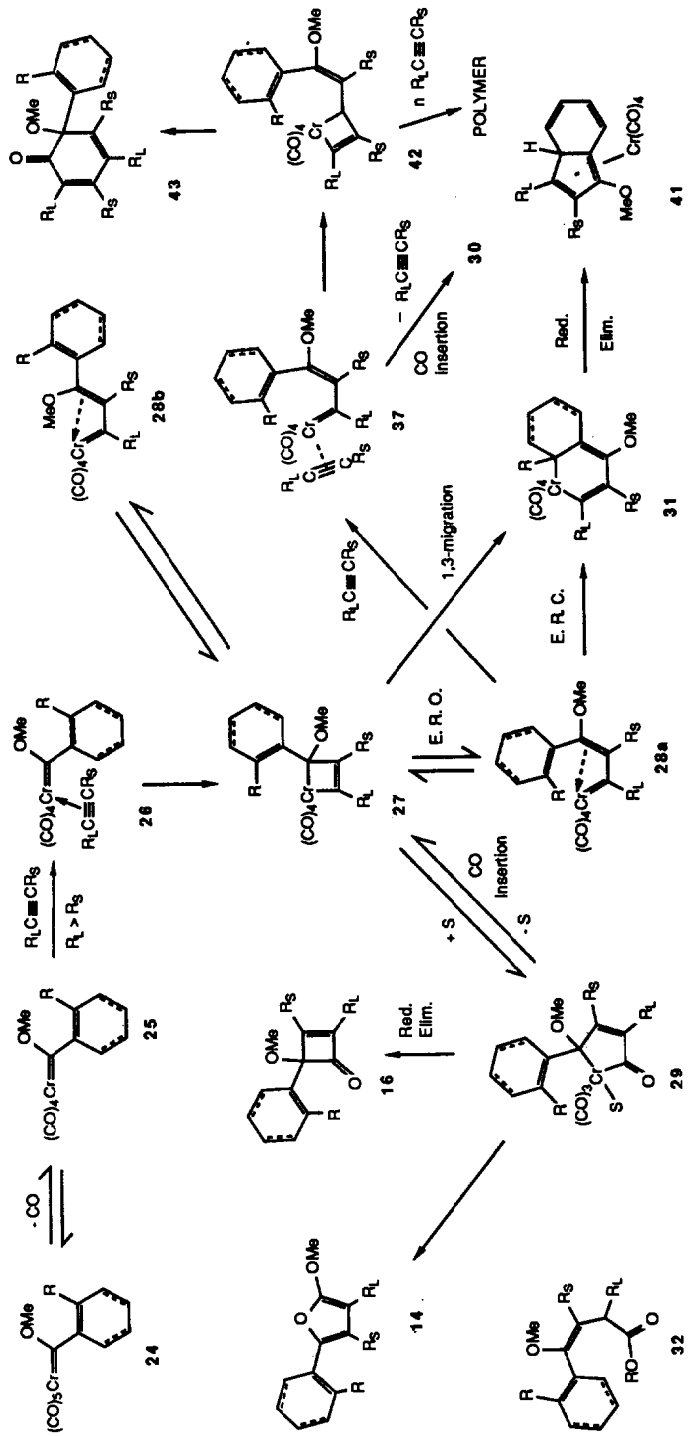
The results of these experiments reveal that the optimal solvents for the benzannulation reaction are those with low coordinating ability. With the exception of acetylenes that are disubstituted with large groups (diphenylacetylene and 1-butylmethylacetylene, series b and f), the benzannulation reactions in hexane are either comparable with or superior to the same reactions in THF (entries 6 and 7, 9 and 10, 12 and 13, 17 and 18, 22 and 24), and in most cases vastly superior to the same reactions in acetonitrile. The reaction of complex **9** with diethylacetylene in hexane resulted in clean formation of the quinone **17b** in 84% yield (along with a 14% yield of biphenyl), whereas the same reaction in THF gave an 88% yield of **17b**. The reaction of complex **9** with 1-pentyne gives a higher yield of the quinone **17d** in hexane (80%) than in THF (73%). The reaction of complex **5** with 1-pentyne gives a 74% yield of the quinone **17h** in THF (entry 22) and 88 and 90% yields in hexane and benzene, respectively (entries 24 and 25). The solvent studies outlined in Table 2 reveal yet another discrepancy between the reactions of the *o*-methoxyphenyl complex **5** and the phenylcarbene complex **9**. The reaction of the *o*-methoxy complex **5** with diethylacetylene in acetonitrile gives no benzannulated product (quinone **17a**) but instead gives reasonable selectivity for the cyclobutenone **16a** (43%), whereas, the phenylcarbene complex **9** gives the quinone **17c** as the major product (38%) along with a smaller amount of the cyclobutenone **16c** (23%) (Scheme 3). However, since the same acetylene is used in each case, the question is now reduced to the role of the *o*-methoxy group in affecting product distribution. At this point, the mechanism of the reaction of chromium carbene complexes with acetylenes must be considered.

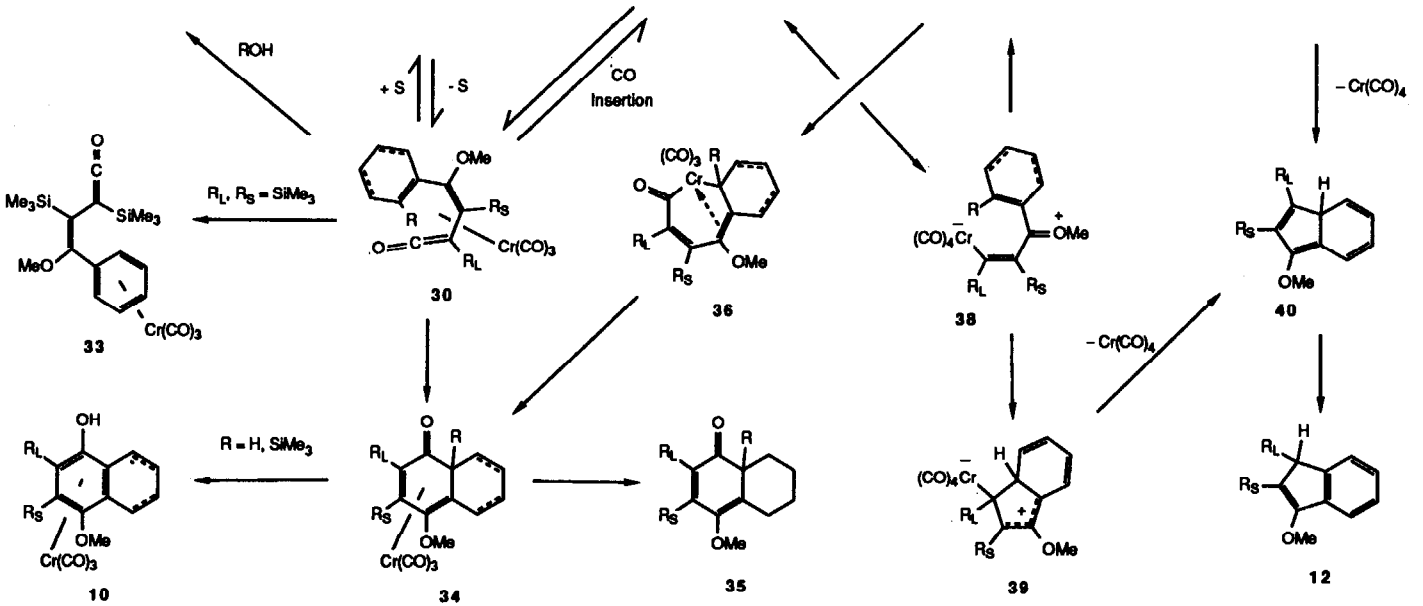
A composite of some of the mechanisms [19,20] that have been previously proposed to account for the various products from the reaction of chromium carbene complexes with acetylenes is presented in Scheme 4. The kinetics of the reaction of the phenyl carbene complex **9** with diphenylacetylene in butyl ether have been investigated (exclusive formation of **10b** reported) and it was found that the reaction was first order in carbene complex and zero order in acetylene and it was found that the rate-limiting step was the first step of the reaction which involves the dissociation of a carbon monoxide ligand, and thus all subsequent steps to product **10** are fast [19]. All of the mechanisms that have been proposed for this reaction, invoke subsequent coordination of an alkyne and rearrangement to the chromacyclobutene intermediate **27**. The isolation of metallacyclobutenes from the reaction of an alkyne and a transition metal–carbon double-bonded species is precedented in the case of titanium [21], and some evidence is available for the case of tungsten [22]. There are two mechanistic pathways to account for the formation of the benzannulated product **10** from the chromacyclobutene intermediate **27**. However,



Scheme 3

the data available in the literature to date are not in conflict with either mechanism. The two mechanisms differ in the order of the two key transformations that are required for the conversion of **27** to **10**; carbon monoxide insertion and cyclization to the phenyl substituent on the carbene carbon. Both mechanisms, as taken from the literature, invoke an electrocyclic ring opening of the chromacyclobutene **27** to give the new vinylcarbene complex **28a**. In both cases this intermediate was written as a 16-electron species, however, it may very well satisfy the degree of unsaturation by chelation of the double bond to give an η^1,η^3-complex that has precedent in a number of iron and tungsten complexes [23,28]. In the mechanism proposed by Casey [20], the vinylcarbene complex intermediate **28a** undergoes an electrocyclic ring closure to give the chromacyclohexadienyl intermediate **31**, which then undergoes carbon monoxide insertion and reductive elimination to give the coordinated cyclohexadienone intermediate **34**, which in the case of hydrogen and silicon [2f] give rise to the aromatized complex **10**, and in the case where R is a group of low migratory propensity, the free cyclohexadienone **35** [24]. In the mechanism proposed by Dötz [19], carbon monoxide insertion occurs before cyclization to give the η^4-vinyl ketene complex **30**, which then undergoes electrocyclic ring closure to give the cyclohexadienone complex **34**. Support for Casey's mechanism comes from the fact that the intermediacy of the chromacyclohexadiene **31** would also nicely explain the formation of non-carbon monoxide inserted products (indenes). However, it has recently been suggested by Yamashita that indenes may be formed via the zwitter-


24
25
26
27
28a
28b
29
30
31
32
37
41
42
43
14
16
- CO
R_L C≡CR_S
R_L > R_S
E. R. O.
E. R. C.
1,3-migration
+ S
- S
CO Insertion
Red. Elim.
Red.
Elim.
n R_L C≡CR_S
POLYMER

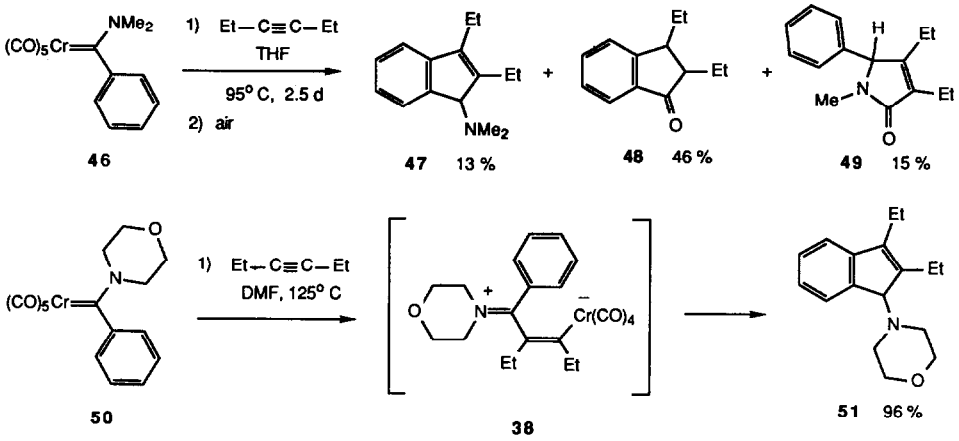

ROH
+ S
- S
CO
Insertion
- Cr(CO)4
RL, RS = SiMe3
R = H, SiMe3
- Cr(CO)4
30
33
36
38
40
10
34
35
39
12

Scheme 4

ion **38** and thus the intermediacy of **31** would not be necessary to account for indene formation [7]. The zwitterion **38** will be discussed in more detail below. Casey's mechanism is also supported by the very recent isolation and characterization of the first example of a metallacyclohexadiene (for platinum), and also the preparation of an η^4-cyclohexadienoneiron tricarbonyl complex (corresponding to the intermediate **34** in Scheme 4) through the suggested intermediacy of a metallacyclohexadiene intermediate [25]. Support for Dötz's mechanism is likewise circumstantial and includes the isolation of vinyl ketenes of the type **33** (only with silyl-substituted acetylenes [24,26]), the isolation of ketene trapping products with alcohols [11], and also with alkenes [27], and the isolation of an η^4-vinyl ketene complex of cobalt from the reaction of a cobalt carbene complex and an acetylene [13]. However, the body of experimental observations made to date cannot be called upon to rule out either Casey's or Dötz's mechanism. Furan formation has been proposed to proceed via the metallacyclopentenone intermediate **29** (a tautomer of the vinyl ketene complex **30**) [13], and cyclobutenone formation can be reasonably invoked to occur via reductive elimination from this same intermediate [19b]. The two-alkyne annulated products of type **43** have been observed from the reaction of carbene complexes and alkynes, and without considering the detail here, it is likely that they are the end result of the reaction of either of the intermediates **27** or **28a** with a second equivalent of acetylene [18]. Other transformations that must be considered are the direct formation of **31** via a 1,3-migration in **27**, and carbon monoxide insertion in **27** to give **29** and thus an alternative entry into the vinyl ketene complex **30**. A closely related observation of carbon monoxide insertion into a titanocyclobutene has recently been described [14]. Also, reversible carbon monoxide insertions have been observed for isolable vinyl ketene complexes of iron [28] and cobalt [13] corresponding to complex **30** in Scheme 4, and thus the possibility of the equilibration of the four intermediates **27**, **28**, **29**, and **30** must be considered.

With regard to factors that favor indene formation, we found that the reaction of the dimethylamino-substituted phenylcarbene complex **46** with diethylacetylene in THF gave the indene products **47** and **48** in a total of 59% yield, and a small amount of the lactam **49**. The higher thermal requirement for this reaction compared to the corresponding reaction of the complex **9**, is due to the decreased lability of the carbon monoxide ligands. The amino-substituted complexes and highly coordinating solvents such as DMF both tend to favor the formation of indene products, and this was brought together in a recent communication by Yamashita in which synthetically useful yields of a number of indenes could be obtained from the reaction of aminocarbene complexes and alkynes in DMF at 125°C [7]. The morpholino complex **50** gave a 96% yield of the indene **51**. Yamashita proposed a mechanism for indene formation that involves the zwitterion **38** undergoing a Nazarov cyclization to give the intermediate **39** (Scheme 4) which then loses $Cr(CO)_4$ to give the indene. At this point neither of the two mechanisms for indene formation indicated in Scheme 4 (via intermediates **31** or **38**) can be ruled out. The intermediacy of **38** in indene formation is quite attractive to consider since it may very well be the more important resonance description of the intermediate **28a** (as a 16-electron complex without the coordinated double bond).

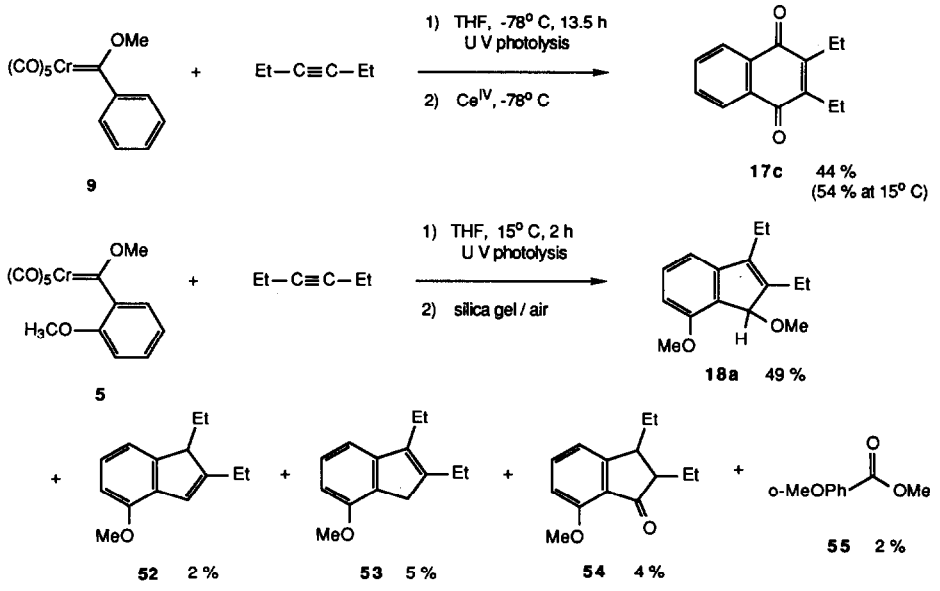
Indene products were also observed under photochemical conditions in the case of the *o*-methoxy complex **5** (Scheme 6). It is known that carbon monoxide ligands of pentacarbonylcarbene complexes of the group 6 metals can be photochemically



Scheme 5

induced to dissociate [30a], and since the rate limiting step of the reaction of acetylenes with these complexes is initial loss of CO, it should be possible to accelerate the benzannulation reaction by photolysis. The reaction of complex **9** with diethylacetylene in THF thermally requires 24 h at 45 °C, but under irradiation with a 450 watt Hanovia medium pressure Hg lamp, the reaction is complete in 3 h at 15 °C, and in 13.5 h at −78 °C (lower light intensity). The yields of the naphthoquinone **17c** are lower than for the thermal reaction, however, the remainder of the mass balance was not accounted for as this reaction was screened only for quinone formation. The photochemical reaction of complex **9** with diphenylacetylene in THF at 15 °C gave a 37% yield of the quinone **17b** and a 3% of the indenone **19b**. In the photochemical reaction of the *o*-methoxyphenyl complex **5** with diethylacetylene no quinone products were observed. This reaction was highly selective for indene formation and only the four indenes indicated in Scheme 6 were isolated from this reaction. The 2% yield of methyl benzoate isolated from this reaction was presumably due to inadvertent oxidation of the carbene complex **9**. The relationship between the *o*-methoxy group and the ultraviolet radiation is not understood at this time, but its connection with indene formation is quite interesting particularly with regard to the concentration studies in Table 4.

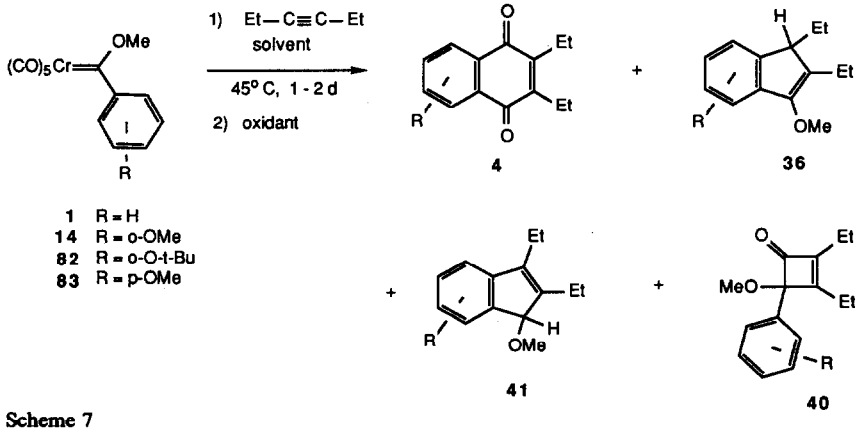
Returning to the reaction of the *o*-methoxyphenyl complex **5** with diethylacetylene in acetonitrile (Scheme 3), the role of the *o*-methoxy group in affecting the product distribution will now be considered. The *o*-methoxy complex **5** gives no quinone and the cyclobutenone **16** is the major product. In the absence of the methoxy group, the complex **9** gives the naphthoquinone **17** as the major product, and the cyclobutenone is obtained as a minor product. The effect of the methoxy group could have electronic origins, or it could be due to intramolecular chelation to the metal. The source of the effects of the methoxy substituent can be probed by comparing the reactions of the *o*-methoxyphenyl complex **5**, the *o*-t-butoxyphenyl complex **56**, and the *p*-methoxyphenyl complex **57**, with those of the unsubstituted phenyl complex **9**. The reactions of the *o*-t-butoxyphenyl complex **56** should be less influenced by chelation effects than should the reactions of the *o*-methoxyphenyl complex **5** due to the greater steric bulk of the ether substituent, however, the



Scheme 6

electronic effects will be the same. The *p*-methoxyphenyl complex **57** cannot have any chelation effects and should have resonance effects similar to that of the *o*-methoxyphenyl complex **5**.

The results from the reactions of complexes **5**, **9**, **56**, and **57** with diethylacetylene in both THF and in acetonitrile are indicated in Table 3. All four complexes give highly selective reactions for naphthoquinone formation in THF, and the cyclobutenone **16** is not observed for any of these complexes in THF. The ratio of naphthoquinone to cyclobutenone (**17**/**16**) for the reaction of the unsubstituted complex **9** in acetonitrile is 38/23. This ratio drops to $< 2/43$ for the *o*-methoxyphenyl complex **5**, and the value of 24/23 for the *o*-t-butoxyphenyl complex **56**



Scheme 7

Table 3

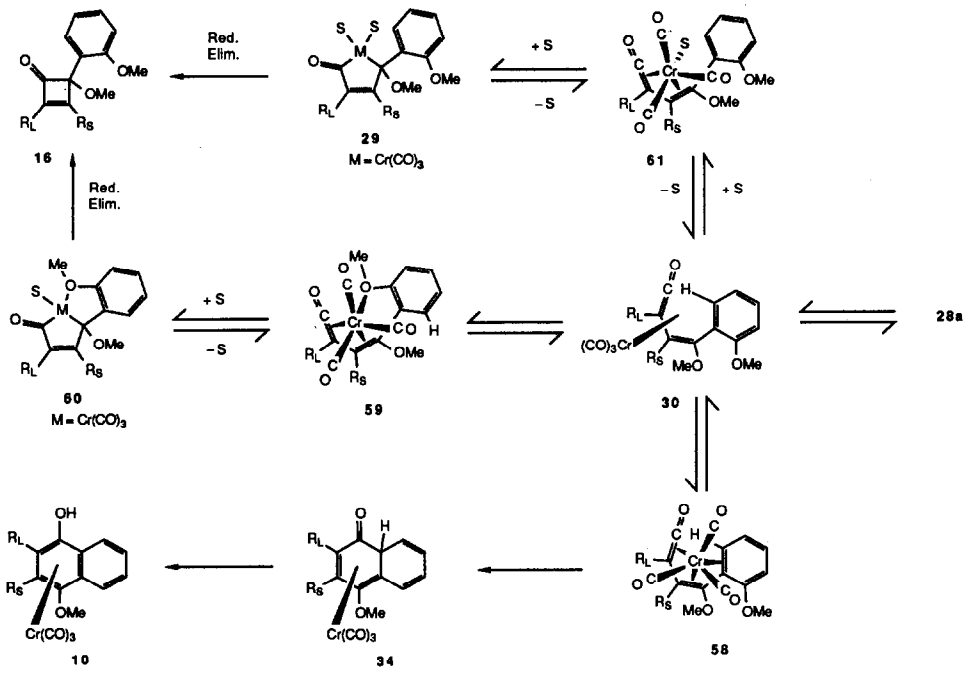
Reaction of substituted aryl complexes with diethylacetylene

series	carbene complex	R	solvent	oxidant	isolated yields (%) 17	12	18	16
c	9	H	THF	Ce^{IV}	88	≤0.3[a]	≤0.3[a]	_[b]
		H	CH_3CN	Fe^{III}	38	8	5	23
a	5	o-MeO	THF	Ce^{IV}	55-65	_[c]	18-26	≤3
		o-MeO	CH_3CN	air	<2	5	12	43
k	56	o-^{t}BuO	THF	Ce^{IV}	72	<2	4	_[b]
		o-^{t}BuO	CH_3CN	Fe^{III}	24	6	12	23
l	57	p-MeO	THF	Ce^{IV}	85[d]			
		p-MeO	CH_3CN	Ce^{IV}	44	13	6	4
		p-MeO	hexane	Ce^{IV}	80[d]			

[a] Determined by capillary GC with diphenylacetylene as internal standard. [b] Not detected by TLC or ^{1}H NMR. [c] A 4% yield of indenone **19a** was isolated from this reaction. [d] Reactions screened only for quinone **17l**.

represents a near restoration to that of the value for the unsubstituted complex **9**. The *p*-methoxyphenyl complex **57** gives a 44% yield of the quinone **17l** in acetonitrile along with a small amount (4%) of the cyclobutenone **16l**. The data in Table 3 suggest that the effect of the *o*-methoxy group on the distribution of quinone and cyclobutenone products from the reaction of the complex **5** with diethylacetylene in acetonitrile is due to chelation and not to the electronic properties or steric effects of the methoxy group.

Cyclobutenone formation is favored in solvents with strong coordinating properties (DMF and HMPA) or in solvents with moderate coordinating ability and small size (acetonitrile), and the presence of an *o*-methoxyl group on the phenyl substitutent of carbene complex also favors cyclobutenone formation owing to chelation by the methoxy group. The fact that the effects of acetonitrile solvent and the *o*-methoxy group taken together give a greater preference for cyclobutenone formation than either one individually (entry 4, Table 3), suggests that cyclobutenone formation requires the coordination of two molecules (solvent or chelated substituent) to the metal center. A more detailed consideration of the intermediates in Scheme 4 that may be responsible for the partition between naphthalene and cyclobutenone formation according to the mechanism proposed by Dötz for naphthalene formation [19] (**27** → **28a** → **30** → **34** → **10**) is presented in Scheme 8. The 16-electron η^4-vinyl ketene complex **30** is the branchpoint in this mechanism that leads to naphthalene and cyclobutenone formation. In the absence of a coordinating group, the metal can coordinate to one of the double bonds of the phenyl ring to give the fully saturated η^6-phenyl vinyl ketene complex **58** which then upon electrocyclic ring closure and tautomerization accounts for the formation of the naphthalene complex **10**. The 16-electron vinyl ketene complexed intermediate **30**



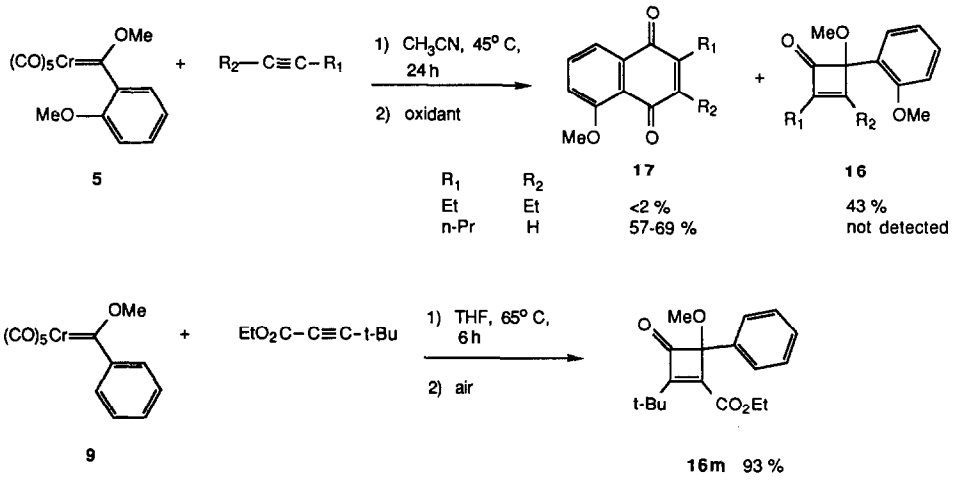
Scheme 8

could also satisfy the unsaturation by coordination of a solvent molecule to give the saturated intermediate **61**, or by chelation to a neighboring methoxy group to give the saturated intermediate **59**. In the latter case, it can be seen that chelation of the methoxy group is not sufficient for cyclobutenone formation; none of the complexes in Table 3 produce cyclobutenones in THF. The mechanism can be fitted to the data if it is proposed that a solvent molecule is required for the conversion of the chelated η^4-vinyl ketene complex **59** to the chelated η^2-metallacyclopentenone intermediate **60**, from which cyclobutenone could be obtained by a reductive elimination [30h]. A phosphine induced conversion of an η^4-bisketene cobalt complex to an η^2-cobaltacyclopentenedione has been reported [30b], however, we found that the ratio of **17c/16c** is essentially unaffected by the presence of two equivalents of triphenylphosphine which was added to the initial reaction mixture in acetonitrile. Cyclobutenones are observed from reactions in coordinating solvents in the absence of chelating groups (Table 2, entries 3, 8, and 16), thus suggesting a parallel pathway involving the disolvated η^2-metallacyclopentenone complex **29**. This mechanism thus explains why in most cases the benzannulated product (naphthalene complex **10**) is observed with highest selectivity when the solvent is of poor coordinating ability (particularly if intermediate **28a** in Scheme 4 is an 18-electron species internally coordinated to the double bond). Carbon monoxide insertion into intermediate **28a** gives the unsaturated vinyl ketene complex **30** which in a non-coordinating solvent has no option but to internally coordinate to give the facial η^6-ketene complex **58** and the benzannulated product **10**.

These results do not rule out Casey's mechanism for naphthalene formation [20] (**27** → **28a** → **31** → **36** → **34** → **10**), but rather give an indication of some of the

details of the steps that lead from the vinyl ketene complex **30** to the cyclobutenone **16**, and the same conclusion would be reached independently of the actual mechanism by which the naphthalene products were formed. These solvent effects could be interpreted according to Casey's mechanism by considering that the 16-electron vinyl ketene complex **30** could be in equilibrium with the 18-electron intermediate vinyl carbene complex **28a** (double bond internally chelated) which would then be the branch point between cyclobutenone and naphthalene formation. The chromacyclobutene intermediate **27** (Scheme 4) is a third possibility for the branch point between cyclobutenone and naphthalene. There are two possibilities by which the product distribution can be accounted for at this branch point. The first is that there exists a competition between carbon monoxide insertion to give **29** and ring opening to give **28a**. Alternatively, the product distribution may be dependent simply on the direction of ring-opening of **27** which could give either **28a** or **28b**. Intermediate **28b** could undergo carbon monoxide insertion to give a vinyl ketene complex diastereomeric with **30** in which cyclization to the aromatic ring was geometrically impossible, but for which cyclobutenone formation via intermediate **29** (Scheme 8) is possible. Neither this study nor the literature provide any data to allow comment on these possibilities at this time.

Another factor that has influence on the partitioning of the intermediates in Scheme 8 is the size of the substituents of the acetylene. The reaction of complex **5** with diethylacetylene in acetonitrile gives none of the quinone **17a** and a 43% yield of the cyclobutenone **16a**, whereas the same reaction with 1-pentyne gives no cyclobutenone and a 57–69% yield of the naphthoquinone **17h** (entry 23, Table 2). There is a correlation of the yields of naphthoquinone **17** from the data in Table 2 with the steric bulk of the acetylene substituents (R^1 and R^2). Each of the acetonitrile reactions in Table 2 in which the yield of the quinone **17** drops to zero is with a disubstituted acetylene with bulky substituents (entries 3, 16, and 19). A small increase in the yield of quinone **17** is observed upon changing dimethylacetylene for diethylacetylene (entries 19 and 21). With monosubstituted acetylenes, cyclobutenone formation is not observed in acetonitrile for either complex **5** or **9** (entries 11 and 23). These results can be interpreted in terms of the intermediates in Scheme 8 in either of two ways. First, increased steric interactions between the acetylene substituents (R_L and R_S) would be expected to favor reductive elimination from **29** or **60** and formation of the cyclobutenone **16** due to the opening of the angles between the substituents on a double-bond in a four membered ring. Alternatively, steric interaction between the substituents on the acetylene and the chromium tricarbonyl metal fragment [30g] would be expected to favor the η^2-complexed intermediates **29** and **60** rather than the η^4- and η^6-complexed intermediates **30**, **59**, **61**, and **58**. An additional observation linking the steric bulk of the acetylene with cyclobutenone formation comes from the reaction in entry 14 of Table 2. This is the only reaction that we have observed in which a cyclobutenone is obtained in an ethereal solvent and it occurs with t-butylmethylacetylene. At the time this was the only reaction that was known that gave a cyclobutenone in an ethereal solvent, except where cyclization to the benzannulated product was blocked [12]. However, it has been recently reported that the phenyl complex **9** will react with ethyl-4,4-dimethyl-2-pentynoate to give the cyclobutenone **15m** in 93% yield [4a]. It is interesting that in this study by Yamashita, the only reaction that was reported to give a cyclobutenone was for the reaction involving the acetylene with the bulkiest substituent.

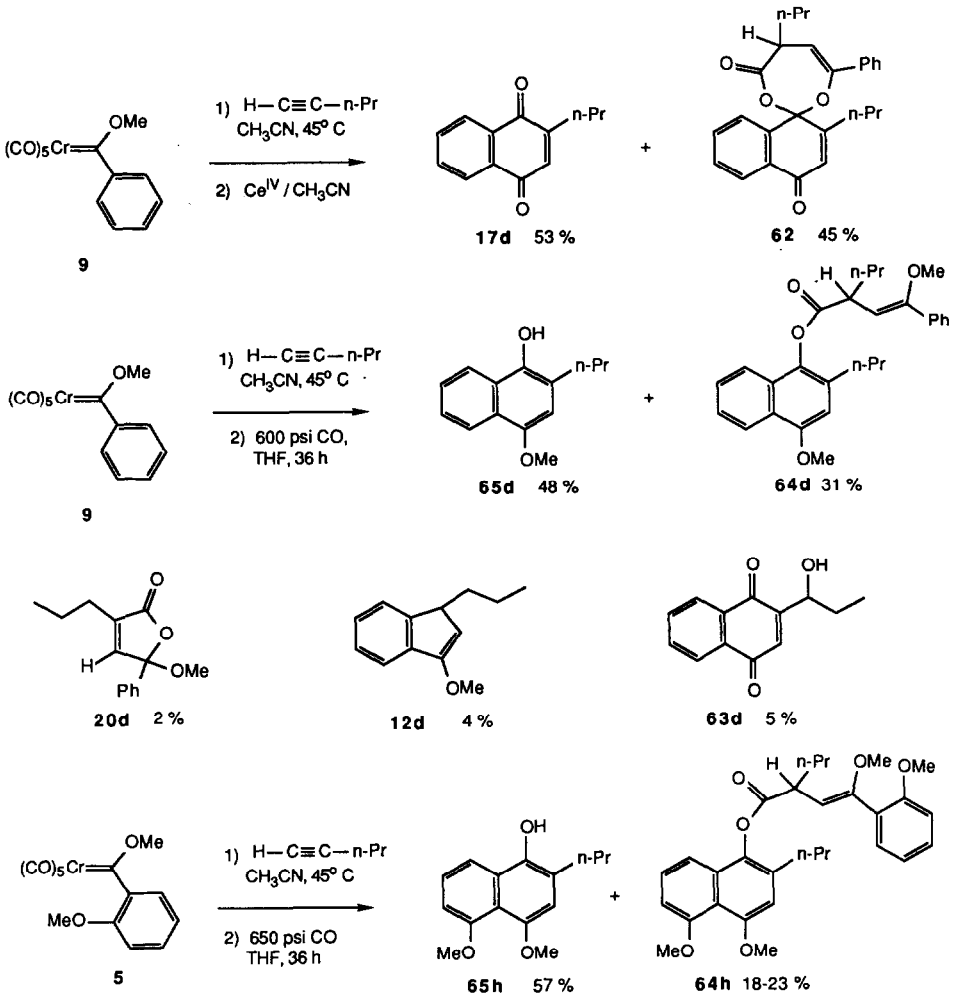


Scheme 9

In all of these studies, a cyclobutenone product has not been observed from a reaction with a terminal acetylene. The reactions of complexes **5** and **9** with 1-pentyne in acetonitrile as indicated by the data in Table 2 gave the quinones **17d** and **17h** in moderate yields. Considerable effort has gone into accounting for the mass balance of these reactions particularly with regard to the possibility that cyclobutenone was formed during these reactions but was destroyed during the workup with ceric ammonium nitrate (CAN). Scheme 10 indicates the other products that are formed in these reactions and some of the by-products whose formation is dependent on the nature of the oxidative workup. However, products corresponding to the cyclobutenones **16d** and **17d** could not be found in either of these reactions.

If the crude mixture from the reaction of the phenyl complex **9** and 1-pentyne in acetonitrile is oxidized with CAN in acetonitrile a second product is obtained that is tentatively assigned as the quinone mono-acetal **62**. If the solvent is first removed from the crude reaction mixture and replaced by hexane prior to oxidation by CAN, the α-hydroxylated quinone **63d** can be obtained in 5% yield in addition to the other products [30i]. If the solvent is replaced by THF prior to oxidation by CAN, the lactone **20d** can be separated from the rest of the products in 2% yield. When no oxidant is used and the crude mixture is treated with 600 psi of carbon monoxide (or simply by oxidation with air) the ketene trapping product **64d** is obtained in 31% yield along with the phenol **65d** and a compound that is tentatively assigned as the indene **12d** in 4% yield. Again, no evidence for a cyclobutenone could be obtained by TLC or ^{1}H NMR of the crude reaction mixture. The variable yields for the quinone **17d** may reflect the degree to which the ketene trapping product **64d** is oxidized to the quinone **17d**. Oxidation of **64d** in THF with CAN gave a 15% yield of **17d**, a 31% yield of **62**, and none of the lactone **20d**. Ketene trapping products of this type have been observed before [4a,30f], and the stereochemistry about the double bond was assigned by correlation of the chemical shift of the vinyl hydrogen with both the *cis*- and *trans*-isomers of known related compounds [30f].

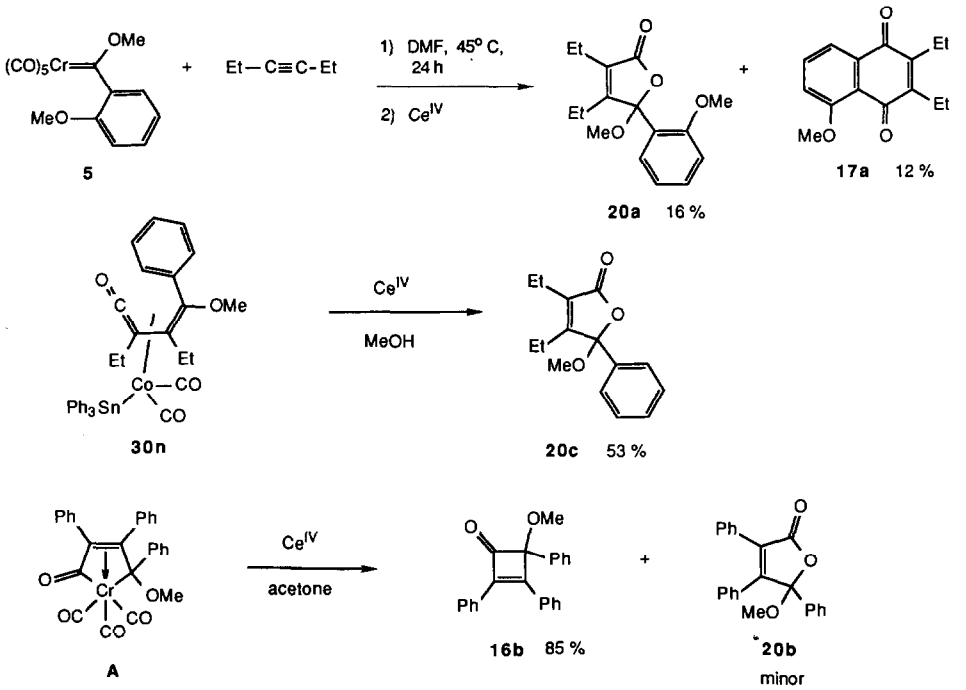
The same reaction of complex **5** upon non-oxidative workup with carbon monoxide gave the ketene trapping product **64h** in 18–23% yield, and the naphthol



Scheme 10

65h which was quantified after purification by oxidation to the quinone **17h**. Again, no evidence for cyclobutenone products could be obtained by TLC or ^{1}H NMR of the crude reaction mixture or upon chromatographic separation of the components visible on TLC by short-wave UV or development with polyphosphomolybdic acid.

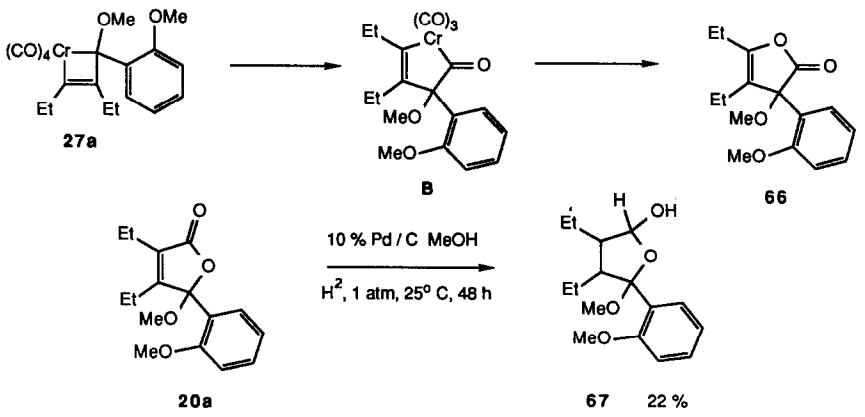
The isolation of the lactone **20a** from the reaction of complex **5** and diethylacetylene in DMF was quite curious (Table 1). The lactone **20a** was isolated in 16% yield from the crude reaction mixture after an oxidative workup that employed ceric ammonium nitrate. Also formed in the reaction were the quinone **17a** (12%) and the indenone **19a** (~ 10–15%). The isolation of the lactone **20a** under oxidative conditions suggest the possibility that an η^4-vinyl ketene chromium complex of the type **30** (or the tautomeric equivalent **29**, Scheme 4) may be present in the crude reaction mixture prior to treatment with the oxidant. We have previously reported that the η^4-vinyl ketene cobalt complex **30n** can be oxidized with ceric ammonium nitrate in methanol to give the related lactone **20c** [13]. The minor component obtained from



Scheme 11

the reaction of the phenyl carbene complex **9** and diphenylacetylene (Scheme 1) was tentatively identified as the internally chelated chromacyclopentenone **A** shown in Scheme 11. It was further reported that this organometallic product could be oxidized by ceric ammonium nitrate in acetone to give the cyclobutenone **16b** and a small amount of the lactone **20b** [5].

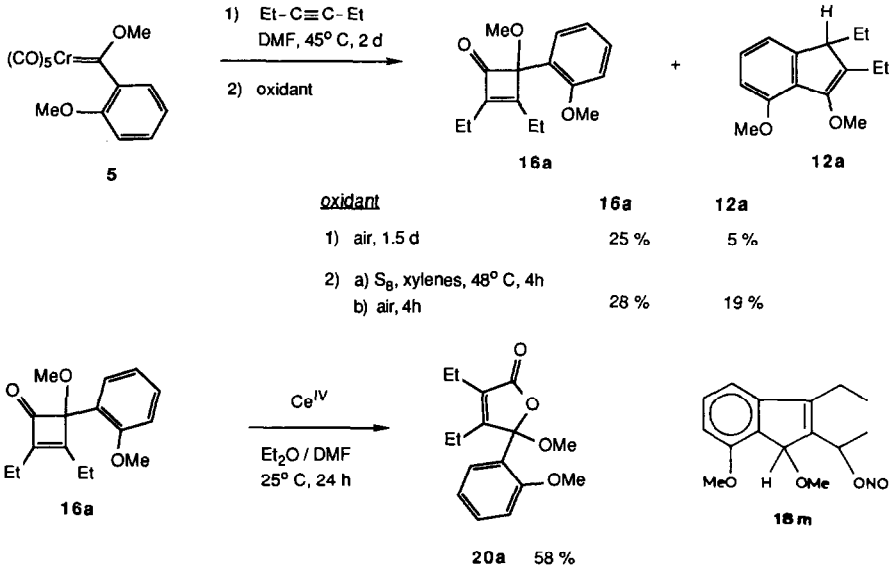
If the lactone **20a** is the result of the direct oxidation of an organometallic intermediate, then the structure of this lactone could provide some information about the structure of the organometallic intermediate. An alternative structure for lactone **20a** is the lactone **66** and both are consistent with the ^{1}H NMR spectrum of the product obtained from this reaction. Lactone **66** would not be expected to arise from the oxidation of a metallacycle of the type **A**, but rather from a chromacyclopentenone of the type **B** [14]. The sites of unsaturation in **B** may be satisfied by coordination to the solvent, DMF. The formation of intermediate **B** would be possible by a carbon monoxide insertion into the metallacyclobutene intermediate **27a** as outlined in Scheme 12. There is precedent for a carbon monoxide insertion into the metal-sp^3-carbon bond of a metallacyclobutene (for titanium [14] as opposed to the metal-sp^2-carbon bond as indicated in Scheme 4 (**27** to **29**). The infrared spectrum of the isolated lactone is most consistent with the the structure **20a**, as the carbonyl absorption (CO, 1755 $cm^{-1}/CHCl_3$) is approximately 50 cm^{-1} too low for the structure **66** [15]. Additional support for the structure **20a** was obtained from hydrogenation experiments. Heterogeneous hydrogenation of the isolated lactone with 1 atm of hydrogen over 10% palladium on carbon gave a number of products. The major product was not completely characterized, but was



Scheme 12

determined to have lost a methoxy and to have suffered partial reduction of the aromatic ring. The second major product was isolated and found to have spectral data consistent with the lactol **67**. The lactol proton was found to be a doublet (δ 4.60 ppm, d, 1H, J 7.8 Hz), whereas, the lactol proton in the corresponding compound derived from lactone **22a** would be expected to be a singlet. The lactone isolated from the DMF reaction thus appears to have the structure **20a** and if it is derived from an organometallic intermediate, it would be from complex A, or intermediate **29** in Scheme 4.

With the assumption that an organometallic complex of the type A was formed from the reaction of carbene complex **5** and diethylacetylene in DMF, other reagents were employed in an attempt to trap and provide further evidence for this metallacycle due to its anticipated instability. It was curious to find that the use of other oxidants in the workup of the reaction mixture in DMF did not result in the isolation of the lactone **20a**, but rather in the isolation of the cyclobutenone **16a** instead. When the crude reaction mixture was stirred in air for 36 h and the products separated, only the cyclobutenone **16a** and the indene **12a** were obtained. The crude reaction mixture was also heated in xylenes with elemental sulfur at 48 °C before exposure to air in an attempt to incorporate sulfur into the metallacycle A [16]. However, after opening to air, only the cyclobutenone **16a** and the indene **12a** could be isolated from the reaction mixture (no attempt was made to isolate the phenol corresponding to **17a** in this case). It was therefore demonstrated that the lactone **20a** was only formed when the crude reaction mixture in DMF was oxidized with ceric ammonium nitrate. A possible explanation is that the cyclobutenone **16a** will undergo a Baeyer–Villager type oxidation with cerium(IV) in DMF but not in any other solvent [17]. Cyclobutenone **16a** proved to be inert to cerium(IV) in diethyl ether at room temperature during the time scale that was used for the oxidations in Table 1 (30–45 min). However, a 25% conversion of **16a** was observed during this time scale when the oxidation was carried out in a 1/1 mixture of DMF and ether (all reaction mixtures in Table 1 were diluted one-fold with ether before oxidation with CAN). Complete conversion of **16a** required 24 h under the conditions employed for the workup of the reaction of complex **5** in DMF. A spiking experiment demonstrated conclusively that the cyclobutenone **16a** can be



Scheme 13

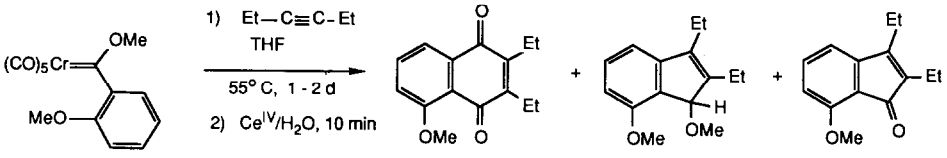
completely converted to the lactone **20a** under the actual reaction conditions. The reaction of complex **5** and diethylacetylene in DMF was repeated under identical conditions except that 0.096 equivalents of **16a** was added to the initial reaction mixture. After the reaction was complete, TLC indicated the absence of the cyclobutenone from the crude mixture and after workup the lactone **20a** was isolated in 27.7% yield which is in excess of the yield obtained without the spike by approximately the amount of cyclobutenone **16a** that was added to the initial reaction. Therefore, from this work there remains no evidence to suggest that the chromacyclopentenone **A** (i.e. intermediate **29**) is a stable product from the reaction of the chromium carbene complex **5** and diethylacetylene in DMF.

In studying the reaction of the *o*-methoxy complex **5** with diethylacetylene we have observed a phenomenon that has not previously been reported for the reaction of carbene complexes with acetylenes. The yields of the quinone **17a** and the indene products (**18a** and **19a**) were found to be variable as indicated by the entry in Table 1 for THF. As a result of an effort to uncover the source of the variability in this reaction it was found that the product distribution is dependent on the concentration of the alkyne. The data summarized in Table 4 reveal that the quinone **17a** is the major product in the presence of excess acetylene. However, the indenes are the major product when the reaction is run with 1.0 equiv. of alkyne, or when the absolute concentration of alkyne is lowered either by dilution or by initiation of the reaction with a deficiency of alkyne and supplementation with additional alkyne over the course of the reaction. The oxidating workup of the reaction of complex **5** with diethylacetylene in THF on some occasions gave a few percent of a compound identified as the nitrate ester **18m**. The side-chain nitrooxylation of methylbenzenes has been reported but only in acetonitrile and only under photochemical conditions [30i]. In all of the reactions of carbene complexes with acetylenes that we have run, the dependence of product distribution on alkyne concentration has only been

noticed for the reaction of the complex **5** with diethylacetylene. Since this was only recently noticed, we have just begun to explore whether or not this phenomenon can be observed for the reactions of other carbene complexes and with other acetylenes. Initial indications are that this phenomenon may not be general.

There appears to be three reasonable points in the mechanism in Scheme 4 at which an alkyne can coordinate and affect the product distribution in favor of the carbon monoxide inserted product (quinone **17a**) over the non-inserted products (indenes **18a** and **19a**). An alkyne could coordinate to the chromacyclobutene intermediate **27** and induce a carbon monoxide insertion [30c,d] to give the chromacyclopentenone intermediate **29**. Alternatively, the alkyne could coordinate to the chromacyclohexadiene intermediate **31** and induce a carbon monoxide insertion to give the intermediate **36**. Finally, a molecule of alkyne could induce a carbon monoxide insertion into the vinyl carbene intermediate **28**. The latter is particularly appealing since coordination of an alkyne to **28a** would give intermediate **37** which is a proposed intermediate in two-alkyne annulation reactions [18] and in the polymerization of acetylenes [30c].

The product distribution could not be substantially affected with the added phosphines, phosphine oxides, or sulfides indicated in Table 4 with the exception of phenyldimethylphosphine. In the latter case, the ratio is increased by a factor of four in favor of the quinone, however, this observation is not as convincing as it might be since the combined yield of the indene and quinone products from this reaction is substantially reduced and several other products were formed which have not yet been isolated and identified. From a consideration of the mechanistic possibilities described above and on the known effect of donor ligands and nucleophiles on carbon monoxide insertions [30c,d] it is to be expected that added



5 **17a** **18a** **19a**

coordinating ligands would favor the carbon monoxide inserted product (quinone). Further studies are in progress concerning the origins of the influence of alkyne on product distribution and on whether this observation holds true for solvents other than THF.

The benzannulation reactions of simple α,β-unsaturated carbene complexes have also found applications in organic syntheses [2f,g,h,i,3b] and the effect of solvent on their reactions has not been previously reported. The data for the reactions of the dihydropyranyl and cyclohexenyl complexes **68** and **71** with various acetylenes and in a number of solvents are presented in Table 5 and Table 6, respectively. The situation with the effect of solvent on the benzannulation reaction of α,β-unsaturated carbene complexes with acetylenes is much simplified; we have never isolated and characterized any product other than the normal benzannulated product (phenol or quinone) from the reaction of any α,β-unsaturated chromium carbene complex with any acetylene and in any solvent. It should be pointed out that these reactions were screened for quinone products and minor products may have been missed, but the yield data show a dramatically lower dependence of the yields of the quinone products on the nature of the solvent.

Table 4

The effect of diethylacetylene concentration on the product distribution from the reaction with complex **5**

entry	[5]	added ligand (equiv)	initial equiv alkyne	initial [alkyne]	reaction time (h)	17a[a]	18a[a]	19a[a]	Total Yield	17a / 18a +19a
1	0.10 M		0.5[b]	0.05 M	63 h	16 %	59 %	9 %	84 %	0.24
2	0.10		1.0[c]	0.10	69	36	59	5	100	0.56
3	0.10		1.7[d]	0.17	34	52	27	4	83	1.68
4	0.10		3.0	0.30	15	54	26	0	80	2.08
5	0.10		9.5	0.95	17	58	14	4	76	3.2
6	0.20		44.3[i]	8.8[i]	24	44[k]	<1	<1	44	≥50
7	0.0050		2.0	0.01	48	5	66	9	80	0.07
8	0.50		1.7[e]	0.85	48	61	18	5	84	2.65
9	0.10	Ph_3P(1.0)	1.7[e]	0.17	48	33	48	9	90	0.57
10	0.10	$PhMe_2P$(1.0)	1.7	0.17	48	27[j]	4[j]	_	31	6.75
11	0.10	Ph_3PO(1.0)	1.0[g]	0.10	43	32	50	6	88	0.57
12	0.10	Bu_3PO(1.0)	1.0[h]	0.10	55	27	30	5	62	0.77
13	0.10	Me_2S(1.0)	1.0[h]	0.10	48	39	43	4	86	0.83

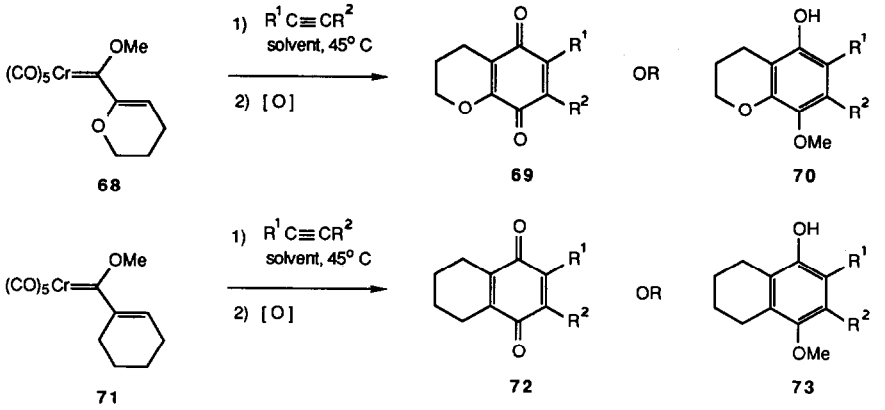
[a] Isolated yields. [b] An additional 0.5 equiv. of alkyne was added after 14.5 h and after 28.5 h. [c] An additional 0.5 equiv. of alkyne was added after 21 h. [d] An additional 1.7 equiv. of alkyne was added after 9.5 h. [e] An additional 1.7 equiv. of alkyne was added after 24 h. [g] An additional 1.0 equiv. of alkyne was added after 12 h. [h] An addition 1.0 equiv. of alkyne was added after 24 h. [i] Diethylacetylene as solvent. [j] Yields estimated from isolated products that were not completely pure as separation was difficult from the many minor products that were produced from this reaction. [k] A 40% yield of ester **55** was also produced in this reaction.

Table 5

Reactions of the alkenyl complex **68**

series	R^1	R^2	solvent	% yield of 69[a]	%yield of 70
a	Et	Et	hexane	79	
	Et	Et	benzene	73	
	Et	Et	THF	73[b]	80[c]
	Et	Et	CH_3CN	64	
b	Ph	Ph	hexane		66[d]
c	nPr	H	THF	67[b]	

[a] Oxidation workup with $(NH_4)_4Ce(NO_3)_6$. [b] Reference 2g. [c] Air oxidation. [d] Oxidation with $FeCl_3$·DMF complex.



Scheme 14

The dihydropyranyl complex **68** will react with diethylacetylene in acetonitrile to give the quinone **69a** and there was no indication of any cyclobutenone from this reaction. Even in the case of the reaction of complex **68** with diphenylacetylene in hexane the selectivity was high for the benzannulated product and there was no indication of any "indene-type" product as might be expected on the basis of the reaction of the phenyl carbene complex **9** and its reaction with diphenylacetylene in heptane (Scheme 1). In the case of the reaction of α,β-unsaturated carbene complexes, the benzannulated products (**10** in Scheme 1) can be converted to the quinones by oxidation of the crude reaction mixture with ceric ammonium nitrate, or to the phenols by oxidation of the crude reaction mixture with ferric chloride-DMF complex [10].

The reactions of the cyclohexenyl complex **71** proceed selectively to give the benzannulated product with diphenylacetylene, diethylacetylene, 1-pentyne, and trimethylsilylacetylene and is unaffected by acetonitrile or methanol as solvents

Table 6

Reactions of the alkenyl complex **71**

series	R^1	R^2	solvent	oxidant	%yield of **72**	%yield of **73**
b	Ph	Ph	THF	Fe[a]		89
a	Et	Et	THF	Ce	65[c]	
	Et	Et	CH_3CN	Ce	56	
c	nPr	H	THF	Ce	61[c]	
	nPr	H	CH_3CN	Ce	69	
	nPr	H	MeOH	Fe[a]		72[d]
d	Me_3Si	H	THF	Air		71[d,c]

[a] $FeCl_3$ DMF complex. [b] $(NH_4)_4Ce(NO_3)_6$. [c] Reference 2g. [d] Less than five weight percent of two minor products was also formed.

although in the latter case a small amount of an uncharacterized product (< 5 weight percent) was obtained which may have been a ketene trapping product [11]. The formation of benzannulated products from the reaction of simple α,β-unsaturated carbene complexes occurs with higher selectivity than the corresponding aryl complexes over a broad range of solvents and alkynes. This can be explained in terms of Dötz's mechanism [19] by the argument that coordination to third double bond in an intermediate corresponding to **58** in Scheme 8 would not require the loss of aromaticity, and in terms of Casey's mechanism [20] by the same argument applied to the electrocyclic ring closure of the vinyl carbene complex intermediate **28a** in Scheme 4 to give the chromacyclohexadienyl complex **31**.

Conclusion

The reactions of arylcarbene complexes with acetylenes are quite sensitive to the nature of the solvent and the substituents of the acetylene. The highest selectivity and efficiency for the benzannulated products are with solvents of low coordinating ability. Solvents with intermediate coordinating ability and small size (acetonitrile) give high selectivity for cyclobutenone formation from reactions with disubstituted acetylenes. Solvents with high coordinating ability give the least selective reactions and a considerable amount of indene products. An *o*-methoxy group on the aryl group of the carbene complex can chelate to the metal center during the course of the benzannulation reaction, and in acetonitrile alter the product distribution in favor of the cyclobutenone product. The results from the study of chelation effects on the partition between cyclobutenone and naphthalene formation are suggestive of the nature of the intermediates involved in cyclobutenone formation, but do not distinguish between various mechanisms for naphthalene formation. The product distribution from the reaction of diethylacetylene with the *o*-methoxyphenyl complex **5** was found to be sensitive to the concentration of the alkyne, a phenomenon not previously observed for the reactions of carbene complexes with acetylenes. In contrast to the reactions of aryl complexes this study reveals that the selectivity of the reactions of α,β-unsaturated carbene complexes of chromium with acetylenes for the formation of benzannulated products is not affected by changes in solvent or substituents of the acetylene. It is anticipated that these studies will be of value in the continued development of the synthetic applications of the reactions of Fischer carbene complexes with acetylenes.

Experimental

Unless otherwise noted all common reagents and solvents were used as obtained from commercial suppliers without further purification. Tetrahydrofuran (THF) and 2,5-dimethyltetrahydrofuran were distilled from sodium benzophenone ketyl immediately prior to use. HMPA was purified by initial fractional distillation, followed by stirring with calcium hydride at 100 °C under reduced pressure, and then final fractional distillation in vacuo. All reactions were carried out under either argon or nitrogen and for reactions involving carbene complexes the reaction mixtures were deoxygenated by the freeze-thaw method (−196 °C/25 °C, 3 cycles). CAN refers to an oxidative workup with 7.5 equivalents of a 0.5 *M* solution of ceric ammonium nitrate in 0.1 *N* aqueous nitric acid. An oxidative workup with ferric

chloride-DMF complex involves treatment with an excess of this reagent [10] (7.5 equivalents) as a THF solution. Unless otherwise specified, the solvents for chromatography and corresponding to the indicated R_f values are a ternary mixture of ether, methylene chloride, and hexane. All melting points and boiling points are uncorrected. Routine proton NMR spectra (δ, ppm) were recorded either on a Bruker 270 MHz or a DS 1000 (Chicago built) 500 MHz spectrometer in $CDCl_3$ with tetramethylsilane as internal standard. The multiplicities of the NMR spectral absorptions are indicated by s, singlet; bs, broad singlet; d, doublet; t, triplet; q, quartet; m, multiplet, and dd, doublet of doublets. The ^{13}C NMR spectra (δ, ppm) were recorded on a Nicolet 200 spectrometer at 50 MHz or on a Varian XL-400 spectrometer at 100 MHz. Infrared spectra were recorded on a Perkin–Elmer model 283 spectrophotometer. Low resolution mass spectra were recorded on a Finnigan 1015 instrument and high resolution mass spectra were carried out on a VG 7070E mass spectrometer or at the Midwest Center for Mass Spectrometry (Nebraska). Elemental Analysis were carried out by Galbraith Lab., Inc.

In none of the reactions reported herein were efforts made to isolate any furan products that might have been formed. The furan products may not be stable to oxidative workup with Fe^{III}, Ce^{IV}, or even with air [14]. Chromatographic separation of the furan product from the crude reaction mixture often requires that the silica gel be pretreated with triethylamine and that the chromatographic solvents be degassed [13]. In addition many of the reactions were screened for the quinone products only and these are so indicated in Tables 1–6.

General procedure for the reaction of aryl chromium carbene complexes with alkynes

Solvent effects on the reactions of the o-methoxyphenylcarbene complex 5 with diethylacetylene

The following procedure for the reaction of complex **5** with diethylacetylene in hexane is typical for the reactions indicated in Table 1 and similar to the procedure previously described with THF solvent [3b*]. A solution of 0.394 g of **5** [3b*,31] (1.15 mmol) and 0.142 g of 3-hexyne (0.20 ml, 1.73 mmol) in 10 ml of hexane was deoxygenated by the freeze-thaw method (−196°/25°C, 3 cycles) in a 25 ml single-necked pear flask that was modified by replacement of the 14/20 joint with a 10 mm threaded teflon high-vacuum stopcock (Kontes No. 826610). The mixture was stirred under argon at 45°C and the progress of the reaction monitored by TLC for the disappearance of complex **5** and of the internally chelated complex **5′** formed in situ [3b*,29]. After 24 h another 1–2 equiv. of diethylacetylene was added. The reaction was complete within 48 h at which time the initial intense red color of the solution due to **5** was nearly discharged and substantial amounts of a brownish-yellow precipitate had formed (the reactions with all other solvents remained homogeneous). The mixture was opened to air, diluted with 20 ml of ether, and oxidized by the addition of 20 ml of a 0.5 *M* solution of ceric ammonium nitrate (CAN) in 0.1 *N* aqueous nitric acid and stirred vigorously for 30 min. The organic phase was separated, washed with water and brine, and dried over $MgSO_4$. After removal of the volatiles, the crude residue was flash chromatographed on silica gel (Merck EM-3920) with a 1/1/4 mixture of ether, methylene chloride and hexane as eluent. The quinone **17a** ($R_f = 0.22$) was obtained in 83% yield (0.232 g, 0.95 mmol) as a yellow solid: m.p. 108.5–109°(ether/hexane); ^1H NMR: δ 1.14 (t,

3H), 1.15 (t, 3H), 2.60 (q, 2H), 2.65 (q, 2H), 4.00 (s 3H), 7.25 (d, 1H, *J* 8.3 Hz), 7.63 (t, 1H, *J* 8.0 Hz), 7.74 (d, 1H, *J* 7.8 Hz); IR (CH_2Cl_2): 3080s, 3005s, 1660s, 1592 cm^{-1}; mass spectrum: *m/e* (% relative intensity) 244 M^+ (20), 229 (45), 201 (55), 115 (58), 76 (100); ^{13}C NMR: δ 13.6, 13.8, 19.7, 20.1, 56.1, 117.0, 118.6, 134.0, 134.2, 145.4, 149.5, 159.0, 184.1, 184.8. Analysis $C_{15}H_{16}O_3$ (C, H).

The above procedure was employed for the solvents benzene, tetrahydrofuran, 2,5-dimethyltetrahydrofuran, 1,4-dioxane, methylene chloride, and nitromethane and the resulting yields of the quinone **17a** are indicated in Table 1. All of these reactions were run with 1.5 equivalents of diethylacetylene, between 0.15–0.20 *M* in complex **5** and 45–50 °C with reaction times varying from 18 h (CH_3CN) to 64 h (HMPA). The reactions in hexane and benzene were observed to be quite clean with the quinone **17a** as the only product obtained from column chromatography on silica gel. In the case of methylene chloride a minor component was eluted from the column ($\leqslant 5\%$) but was not characterized. In the case of benzene, three other components were isolated but were not characterized ($\leqslant 3\%$ each). The reactions in THF indicated in Table 4 were carried out at 55 °C with the general procedure described above with the exceptions indicated in Table 4 and oxidized with CAN in water (no acid). The indene **18a** and indenone **19a** that were isolated from this reaction had ^1H NMR spectra that were identical to those compounds that were obtained from the reactions in acetonitrile and DMF, respectively.

When the reaction of complex **5** with diethylacetylene was carried out in acetonitrile and worked up employing the procedure described above none of the quinone **17a** was obtained as judged by a CAN oxidation of a small aliquot of the reaction mixture, and by a CAN oxidation of a small aliquot of the reaction mixture after the acetonitrile solvent of the aliquot was replaced by ether before oxidation. The reaction mixture was opened to air, diluted with ether and aqueous saturated ammonium chloride. The ether layer was washed with water, brine, and dried over $MgSO_4$. Two components were observed to elute from a silica gel column with a 1/1/10 mixture of ether, methylene chloride, and hexane. The slower moving compound ($R_f = 0.13$) was isolated and identified as the cyclobutenone **16a** (43%) on the basis of the following spectral data: ^1H NMR: δ 1.08 (t, 3H, *J* 7.5 Hz), 1.18 (1, 3H, *J* 7.1 Hz), 2.27 (m, 2H), 2.43 (q, 2H, *J* 7.6 Hz), 3.41 (s, 3H), 3.74 (s, 3H), 6.86 (d, 1H, *J* 8.5 Hz), 6.97 (dt, 1H, *J* 1.0, 7.8 Hz), 7.26 (dt, 1H, *J* 1.2, 7.9 Hz), 7.58 (dd, 1H, *J* 1.4, 7.7 Hz); ^{13}C NMR (50 MHz): δ 11.43, 12.03, 17.17, 20.91, 53.68, 55.60, 98.02, 111.79, 120.94, 125.91, 128.68, 129.37, 154.86, 157.19, 178.40, 193.18; IR (neat): 1758s, 1630m cm^{-1}; mass spectrum: *m/e* (% relative intensity) 260 M^+ (31), 245 (45), 203 (17), 201 (16), 135 (100), 115 (11), 92 (13), 77 (30). Calcd. for $C_{16}H_{20}O_3$ *m/e* 260.1412; measured 260.1420. A minor component ($R_f = 0.19$) was further purified on a 20 × 20 cm 2000 μ preparative TLC plate and isolated (12%) and identified as 1,7-dimethoxy-2,3-dimethylindene **18a** on the basis of the following spectral data: ^1H NMR: δ 1.13 (t, 3H, *J* 7.5 Hz), 1.14 (t, 3H, *J* 7.5 Hz), 2.27 (m, 1H), 2.45 (m, 3H), 3.01 (s, 3H), 3.90 (s, 3H), 5.13 (s, 1H), 6.70 (d, 1H, *J* 8.3 Hz), 6.82 (d, 1H, *J* 7.3 Hz) 7.25 (broad t, 1H, *J* 8 Hz); ^{13}C NMR (100 MHz): δ 14.02, 14.15, 18.36, 18.68, 51.54, 55.38, 81.02, 121.67, 115.58, 126.73, 130.02, 139.73, 143.40, 146.93, 156.06; IR ($CHCl_3$): 2960s, 2930m, 2890w, 2870w, 1605s, 1585s, 1475s, 1460s, 1260s, 1134w, 1080m, 1060m cm^{-1}; mass spectrum: *m/e* (% relative intensity) 232 M^+ (47), 217 (21), 204 (38), 203 (100), 188 (35), 172 (22), 141 (23), 129 (25), 128 (42), 105 (45); calcd. for $C_{15}H_{20}O_2$ *m/e* 232.1463, measured 232.1461.

A second minor component was isolated (5%) and identified as the indene **12a** on the basis of the following spectral data: ^{1}H NMR: δ 0.53 (t, 3H, J 7.4 Hz), 1.11 (t, 3H, J 7.5 Hz), 1.83 (m, 1H), 2.05 (m, 2H), 2.68 (m, 1H), 3.34 (m, 1H), 3.79 (s, 3H), 3.90 (s, 3H), 6.80 (d, 1H, J 8 Hz), 6.99 (d, 1H, J 7.3 Hz), 7.13 (t, 1H, J 7.5 Hz). As indicated in Table 1, this reaction in acetonitrile gives essentially the same outcome (36% of **16a** and 12% of **18a**) when carried out in the presence of 1 atm of carbon monoxide instead of argon.

The crude mixture from the reaction of **5** and diethylacetylene in methanol was oxidized by addition of a solution of excess (7.5 equiv.) of ferric chloride-DMF complex [10] in THF. After workup the two major products from the reaction were isolated and identified as the quinone **17a** (51%) and the indene **18a** (20%). Two other compounds were isolated from the mixture in small amounts ($< 5\%$ each) but were not characterized and could have been ketene trapping products.

The reaction of **5** and diethylacetylene in HMPA was carried out as described above for the reaction in hexane (1.49 mmol of **5** in 10 ml of HMPA). Before oxidation with CAN the reaction mixture was diluted with 50 ml of ether and 10 ml of water. After oxidation, the organic phase was washed several times with water and dried over $MgSO_4$. After removal of the volatiles, the residue was chromatographed on silica gel with a 1/1/8 mixture of ether, methylene chloride, and hexane as eluent to afford four compounds. Three of the four were isolated and identified as the quinone **17a** (12%), the cyclobutenone **16a** (29%), the indene **18a** (6%), and a fourth compound tentatively identified as the indene **12a** (15%) on the basis of its ^{1}H NMR spectrum (see acetonitrile reaction).

The reaction of the o-methoxyphenylcarbene complex 5 with diethylacetylene in DMF

A solution of complex **5** (1.00 g, 3.21 mmol) and 3-hexyne (0.5 ml, 4.82 mmol) in 20 ml of DMF was deoxygenated by the freeze-thaw method. The solution was heated at 45 °C for 48 h in the reaction vessel described in the general experimental. At the end of the reaction $Cr(CO)_6$ had sublimed to the top of the flask and the solution had turned green. The solution was opened to the air, diluted with 20 ml of ether and treated with 10 ml of a 0.5 M solution of cerric ammonium nitrate in 0.1 N aqueous nitric acid. After stirring for 2 h, the organic phase was separated, washed with water and brine and dried over $MgSO_4$. After removal of the volatiles, the residue was flash chromatographed on silica gel with a 1/1/4 mixture of ether, methylene chloride, and hexane as eluent. A number of products were observed that eluted over the range of $R_f = 0.1$–0.3. The major product ($R_f = 0.20$) could be separated from the others by rechromatographing the mixture with a 1/1/6 solvent mixture and was obtained in 16% yield as white prisms and identified as the lactone **20a** on the basis of the following spectral data: m.p. 103–104 °C (hexanes); R_f (1/1/4) = 0.2; R_t (OV-17, 200 °C) 1.88 min; ^{1}H NMR: δ 0.78 (t, 3H, J 7.7 Hz), 1.19 (t, 3H, J 7.4 Hz), 2.06–2.16 (m, 2H), 2.36 (m, 2H), 3.30 (s, 3H), 3.69 (s, 3H), 6.83 (d, 1H, J 8.1 Hz), 6.98 (t, 1H, J 7.7 Hz), 7.32 (dd, 1H, J 1.3, 7.5 Hz), 7.75 (dd, 1H, J 1.4, 7.7 Hz) ppm; ^{13}C NMR (50 MHz): δ 12.08. 13.31, 17.31, 18.90, 50.12, 55.50, 106.75, 111.68, 120.53, 123.85, 128.66, 130.67, 132.61, 157.28, 158.69, 172.76; IR ($CHCl_3$): 1755s, 1600w, 1490m, 1462 m cm^{-1}; mass spectrum: m/e (% relative intensity) 276 M^+ (2), 245 (32), 216 (30), 203 (22), 169 (35), 135 (100), 82 (83), 77 (45), 67 (57). Calcd. for $C_{16}H_{20}O_4$ m/e 276.1361; measured 276.1366.

The next two major components could be identified in the mixture from the

initial chromatography (R_f 0.1–0.3). The indenone **19a** could be separated from the mixture by preparative GC (0.25″ × 8′OV-17 column at 220 °C, ret. time 1.5 min) and was not quantified but was present in a lesser amount than the lactone **20a** (Ret. time 1.88 min, assuming equal response factors). The following data was collected for **19a**: ^{1}H NMR: δ 1.05 (t, 3H, J 7.5 Hz), 1.20 (t, 3H, J 7.7 Hz), 2.26 (q, 2H, J 7.0 Hz), 2.52 (q, 2H, J 7.0 Hz), 3.93 (s, 3H), 6.09 (d, 1H, J 7.0 Hz), 6.77 (d, 1H, J 8.6 Hz), 7.30 (t, 1H, J 7.8 Hz); IR (neat): 1700s, 1595s, 1475s, 910 s cm^{-1}; mass spectrum: m/e (% relative intensity) 216 M^+ (100), 201 (100), 187 (58), 174 (20), 159 (25), 142 (25), 128 (40), 115 (48). Calcd. for $C_{14}H_{16}O_2$ m/e 216.1150; measured 216.1138. Evidence for the presence of the quinone **17a** in the initial chromatography mixture was provided by HPLC (Waters RCM radial pak B, ether/methylene chloride/hexane, 1/1/2, 6.0 ml/min, retention time of **17a** 1.27 min). The yield of **17a** was determined to be 12% by quantification with a standard solution of **17a**.

An attempt at incorporation of sulfur into the products was made by transferring the crude reaction mixture under argon to a deoxygenated suspension of sulfur (10 equiv.) in xylenes (1.5 mmol in 10 ml of solvent) [16]. The resulting mixture was heated at 48 °C for 4 h, opened to the air and stirred at room temperature for an additional 4 h. After the workup described above, the two major products were separated and purified by flash chromatography on silica gel with a 1/1/4 solvent mixture and identified as the indene **18a** (19%) and the cyclobutenone **16a** (28%).

A spiking experiment was performed to determine the stability of the cyclobutenone **16a** to the reactions conditions in DMF and to the ceric ammonium nitrate oxidative workup. The reaction was repeated as described above except that 0.096 equivalents of **16a** was added to the initial mixture. After the reaction was complete, TLC indicated the absence of the cyclobutenone from the crude mixture and after workup the lactone **20a** was isolated in 27.7% yield which is in excess of the yield obtained without the spike by approximately the amount of cyclobutenone **16a** that was added to the initial reaction.

*Hydrogenation of lactone **20a***

A solution of lactone **20a** (55.2 mg, 0.18 mmol) in 10 ml of MeOH was treated with 100 mg of 10% Pd/C and stirred under 1 atm of H_2 at 25 °C for 48 h. The suspension was filtered through celite and then evaporated to dryness. The residue was chromatographed on silica gel with a 1/1/4 solvent mixture. The major product was not completely characterized but its ^{1}H NMR spectrum and mass spectrum indicated substantial overreduction including loss of a methoxyl and partial reduction of the aryl group. A minor product (R_f = 0.14) was obtained (11 mg, 22%) whose spectral data are consistent with the lactol **67**: ^{1}H NMR (500 MHz, CD_3OD): δ 0.68 (t, 3H, J 7.5 Hz), 0.82 (t, 3H, J 7.4 Hz), 1.10–1.20 (m, 1H), 1.25–1.35 (m, 2H), 1.64–1.74 (m, 1H), 1.89–1.94 (m, 1H, becomes a narrower multiplet upon irradiation at δ 4.60), 2.45 (dt, 1H, J 3.4, 9.1 Hz, collapses to a dd upon irradiation at δ 1.90), 3.04 (s, 3H), 3.74 (s, 3H), 4.60 (d, 1H, J 7.8 Hz, collapses to a singlet upon irradiation at δ 1.90), 6.89 (m, 2H), 7.18 (dt, 1H, J 1.2, 8.1 Hz), 7.27 (dd, 1H, J 1.2, 7.4 Hz); mass spectrum: m/e (% relative intensity). 280 M^+ (1), 204 (1), 175 (2), 162 (8), 157 (100), 122 (18), 91 (23), 45 (78).

*The oxidation of the cyclobutenone **16a** with ceric ammonium nitrate in DMF*

A solution of cyclobutenone **16a** (68 mg, 0.26 mmol) in 20 ml of a 1/1 mixture of

DMF and ether was added to 10 ml of a solution of 0.5 *M* ceric ammonium nitrate in 0.1 *N* aqueous nitric acid and the resulting mixture stirred at 25 °C for 1 d. The solution was then extracted with ether, washed with water and brine and dried ($MgSO_4$). After evaporation, the residue was flash chromatographed (1/1/6) and two fractions were obtained. Fraction 1 (42 mg, 0.15 mmol, 58%), $R_f = 0.22$, was a white solid which was identified as the lactone **20a** by comparison of its ^{1}H NMR spectrum with that of the previously characterized lactone **20a**. Fraction 2 (10 mg, 0.036 mmol, 14%) was a colorless oil and was not identified but had the following spectral data: $R_f = 0.16$; ^{1}H NMR: δ 1.06 (t, 3H, *J* 7.6 Hz), 1.11 (t, 3H, *J* 7.4 Hz), 2.39–2.44 (m, 4H), 3.42 (s, 3H), 3.79 (s, 3H), 6.91 (d, 1H, *J* 8.2 Hz), 7.00 (t, 1H, *J* 7.4 Hz), 7.44 (dt, 1H, *J* 1.7, 7.0 Hz), 7.86 (dd, 1H, *J* 1.7, 7.8 Hz); ^{13}C NMR (100 MHz): δ 12.16, 13.47, 21.46, 23.91, 51.44, 55.36, 111.91, 120.61, 126.28, 129.68, 131.22, 124.08, 154.18, 159.07, 168.13; IR ($CDCl_3$) 1707s, 1672s, 1593s, 1315s, 1259s, 1235s, 1198s, 1132s, 1054m, 1027 s cm^{-1}; mass spectrum: *m/e* (% relative intensity) 276 M^+ (5), 247 (7), 217 (6), 217 (6), 215 (12), 135 (100), 136 (9), 92 (7), 77 (15).

The above oxidation of **16a** in DMF was also stopped and worked up after 30 min and the reaction was not complete and the isolated yield of the lactone **20a** was 25%. The same oxidation of **16a** was performed only in ether solvent, and after 30 minutes the reaction was worked up and the ^{1}H NMR, IR, and GC spectra of the crude reaction mixture all indicated the absence of the lactone 20a.

The reaction of the phenylcarbene complex 9 with diphenylacetylene

The reaction of complex **9** [32*] (1.60 mmole) with diphenylacetylene (1.92 mmol) was carried out in acetonitrile (10 ml) according to the general procedure employing an oxidative workup with CAN. The crude polar component ($R_f = 0.06$) was a minor fraction (< 3%) that was not identified. The major product ($R_f = 0.24$) was isolated in 51% yield and identified as the cyclobutenone **16b** as it had ^{1}H NMR and IR spectra identical to that of a compound previously isolated from the reaction in heptane [5]; **16b**: ^{1}H NMR: δ 3.55 (s, 3H), 7.23–7.90 (m, 15H); IR ($CHCl_3$): 1750s, 1600m, 1350m cm^{-1}. A third compound ($R_f = 0.44$, 4%) was identified as the indene **12b** by comparison of its spectral data with those of a compound previously reported from this reaction in heptane [12]; **12b**: ^{1}H NMR: δ 3.97 (s, 3H), 4.88 (s, 1H), 7.04–7.61 (m, 14H); mass spectrum: *m/e* (% relative intensity) 298 M^+ (7), 282 (7), 265 (3), 105 (53), 83 (100), 47 (40). A fourth product ($R_f = 0.33$) was isolated (15%) that was identified as the indene **18b** on the basis of the following spectral data: ^{1}H NMR: δ 3.01 (s, 3H), 5.70 (s, 1H), 7.16–7.62 (m, 14H); mass spectrum: *m/e* (% relative intensity) 298 M^+ (100), 283 (30), 265 (18), 255 (20), 178 (23), 121 (30), 105 (63), 77 (33). The ^{1}H NMR data for **18b** are consistent with that previously reported for this compound [33].

The reaction of complex **9** and diphenylacetylene was also carried out in benzene and THF according to the general procedures and on the same scale. Utilizing the purification procedure above, the reaction in THF provided the quinone **17b** in 59% yield. This quinone had been previously reported from this reaction in n-Bu_2O; **17b**: m.p. 138–140 °C (MeOH) (lit. [5] m.p. 141 °C), ^{1}H NMR: δ 7.08 (m, 6H), 7.23 (m, 2H), 7.24 (m, 6H), 7.80 (m, 6H), 8.20 (m, 2H). The reaction in benzene gave a 36% yield of quinone **17b**, a 21% yield of the cyclobutenone **16b**, and a small amount of a third compound that was not identified, but was determined not to be indene **12b** or **18b**.

The reactions of phenylcarbene complex **9** with diphenylacetylene in the various solvents described above with an oxidative workup with CAN were calibrated by carrying out the same reaction in hexane with a CAN workup and comparing with the same reaction run in heptane (Scheme 2) that had previously been described without an oxidative workup. As can be seen from the data in Table 2, the yields of naphthalene and indene products are comparable. No attempt was made to isolate the small amount of cyclobutenone **16b** or furan **14b** from this reaction. It is our experience that furan products of the type **14b** are destroyed by CAN [13]. The CAN treatment also oxidizes both indene products **12b** and **18b** to the indenone **19b**: m.p. 148–150°C (lit. [34] 149–151°C); ^{1}H NMR: δ 7.12 (d, 1H, J 7.25 Hz), 7.21–7.28 (m, 6H), 7.33–7.40 (m, 6H), 7.56 (d, 1H, J 6.95 Hz); IR ($CHCl_3$): 3070–3029m, 1701s, 1686s, 1604s, 1479m, 1456s, 1438s, 1339s, 1182m, 1077m, 701s; mass spectrum: m/e (% relative intensity) 282 M^+ (100), 265 (12), 252 (48), 240 (12), 178 (15), 165 (10), 126 (17), 105 (87), 91 (14), 77 (48), 69 (22); calcd. for $C_{21}H_{14}O$; m/e 282.1045, measured m/e 282.1033.

The reaction of carbene complex 9 with diethylacetylene

The reaction of complex **9** (2.13 mmol) with diethylacetylene (3.20 mmol) was carried out in acetonitrile (13 ml) according to the general procedure. The reaction was complete in 20 h and the resulting mixture was oxidized with a solution of excess $FeCl_3$-DMF complex in THF for 2 h. After the usual workup, the products were separated on silica gel with a 1/1/20 solvent mixture. The cyclobutenone **16c** was isolated in 23% yield. **16c** (R_f 0.13, colorless oil) ^{1}H NMR: δ 1.15 (t, 3H, J 7.6 Hz), 1.21 (t, 3H, J 7.6 Hz), 2.32 (m, 2H), 2.53 (m, 2H), 3.42 (s, 3H), 7.26 (t, 1H, J 8.1 Hz), 7.32 (t, 2H, J 7.8 Hz), 7.37 (d, 2H, J 7.4 Hz); IR ($CDCl_3$): 2960s, 1750s, 1620s, 1460s, 1095s; mass spectrum: m/e (% rel intensity) 230 M^+ (48), 215 (76), 173 (60), 121 (50), 105 (100), 77 (52). Calcd. for $C_{15}H_{18}O_2$ 230.1307; measured 230.1307. The quinone **17c** (R_f = 0.26) was isolated as a yellow solid in 38% yield. **17c**: m.p. 67–69°C (lit. [35] 72–73°C); ^{1}H NMR: δ 1.16 (t, 6H, J 7.5 Hz), 2.66 (q, 4H, J 7.5 Hz), 7.67–7.72 (m, 2H), 8.06–8.09 (m, 2H); IR ($CHCl_3$): 3063w, 2977s, 2938s, 2874m, 1662s, 1614m, 1596s, 1463s, 1345m, 1329m, 1298s, 1257m. A small amount of a colorless oil (R_f = 0.34) was isolated and tentatively identified as the indene **18c** (5%) on the basis of the following spectral data: ^{1}H NMR: δ 1.18 (t, 6H, J 7.6 Hz), 2.25–2.33 (m, 1H), 2.45–2.53 (m, 3H), 3.03 (s, 3H), 5.02 (s, 1H), 7.15 (t, 1H, J 7.4 Hz), 7.19 (d, 1H, J 7.8 Hz), 7.26 (t, 1H, J 7.7 Hz), 7.44 (d, 1H, J 7.2 Hz); mass spectrum: m/e (% relative intensity) 203 (28), 202 M^+ (95), 187 (66), 174 (63), 173 (100), 158 (85), 141 (59), 128 (54), 115 (57). A fourth compound was isolated and identified as the indene **12c** (8%) on the basis of the following spectral data: ^{1}H NMR: δ 0.60 (t, 3H, J 7.4 Hz), 1.17 (t, 3H, J 7.5 Hz), 1.73–1.83 (m, 1H), 2.0–2.1 (m, 1H), 2.12–2.22 (m, 1H), 2.67–2.75 (m, 1H), 3.39 (t, 1H, J 5.0 Hz), 3.90 (s, 3H), 7.15 (t, 1H, J 7.3 Hz), 7.26 (t, 1H, J 7.4 Hz), 7.29 (d, 1H, J 7.4 Hz), 7.34 (d, 1H, J 7.3 Hz); ^{13}C NMR (100 MHz): δ 8.45, 14.24, 18.01, 22.29, 46.41, 59.88, 117.50, 122.87, 124.25, 126.14, 131.78, 140.88, 145.04, 152.33; IR (neat): 2964s, 1632s, 1465s, 1358s, 1136s, 746s cm^{-1}; mass spectrum: m/e (% relative intensity) 202 M^+ (8), 187 (10), 173 (32), calcd. for $C_{14}H_{18}O$ m/e 202.1358; measured 202.1327.

The distribution of **16c** and **17c** did not change when freshly crystallized triphenylphosphine (2 equiv.) was added to the initial reaction mixture. After the

reaction was carried out and worked up in the same manner, the isolated yields of **16c** and **17c** were 12 and 28%, respectively.

The reaction of complex **9** and diethylacetylene in THF under the same conditions but with a CAN workup gave the quinone **17c** as the exclusive product (88%). Analysis of the crude THF reaction mixture by capillary GC (25 m × 0.32 mm OV-1701, 150°C) with diphenylacetylene as added internal standard revealed ⩽0.3% of the indene **18c** (R_f = 4.86) and ⩽0.3% **12c** (R_f = 3.49). The same reaction in hexane gave the quinone **17c** in 84% yield after workup with CAN along with a small amount (14%) of a white solid that had an R_f value and a ^{1}H NMR spectrum identical to that of an authentic sample of biphenyl.

The reaction of carbene complex 9 with 1-pentyne

The reaction of complex **9** (0.5 mmol) and 1-pentyne (0.75 mmol) was performed in hexane (5 ml) according to the general procedure. The reaction was complete in 72 h at 45°C. After the normal oxidation (CAN) and hydrolytic workup the crude reaction mixture was eluted through silica gel with a 1/1/10 solvent mixture to give two products. The major product was the first to elute (R_f = 0.30) and was identified as the quinone **17d** (80%): yellow solid, m.p. 39°C (lit. [36] m.p. 37–39°C); ^{1}H NMR: δ 1.04 (t, 3H, J 7.4 Hz), 1.65 (Sext., 2H, J 7.6 Hz), 2.57 (t, 2H, J 7.7 Hz), 6.79 (s, 1H), 7.71–7.74 (m, 2H), 8.05–8.10 (m, 2H); IR (CCl_4): 2970m, 1665s, 1615m, 1597m, 1325m, 1302m, 1263m cm^{-1}. The second product was obtained as a yellow oil (R_f = 0.26, 12%) and as of yet has not been identified and for which the the following spectral data have been collected: ^{1}H NMR: δ 0.89 (t, 3H, J 7.3 Hz), 1.06 (t, 3H, J 7.4 Hz), 1.2 (m, 2H), 1.7 (m, 2H), 1.84 (t, 2H, J 8.5 Hz), 2.52 (t, 2H, J 7.8 Hz), 3.19 (s, 3H), 4.99 (s, 1H), 6.93 (s, 1H), 7.30–7.33 (m, 5H); IR ($CHCl_3$): 1700s cm^{-1}; mass spectrum m/e (% relative intensity) 312 M^+ (100), 281 (12), 269 (13), 252 (8), 223 (18), 115 (22), 105 (58), 91 (17), 77 (44).

The reaction of **9** and 1-pentyne were also carried out in THF and acetonitrile and on the same scale and with the same conditions both reactions were complete in 20 h. The THF reaction was relatively clean and gave the quinone **17d** in 73% yield. The crude reaction mixture from the acetonitrile reaction was evaporated to dryness and the residue extracted with 10 ml of hexane and then 2 ml of ether. The combined fractions were oxidized with CAN and after the normal workup the product mixture was eluted on silica gel with a 1/1/10 solvent mixture. The first fraction to elute (R_f = 0.56) had no carbonyl absorption in the IR and by ^{1}H NMR was a mixture of several compounds and if it is assumed all had the same molecular weight as **17d** would all together be a total of 5% yield. The second fraction (R_f = 0.30) was the quinone **17d** in 53% yield. The third fraction (R_f = 0.24) had a carbonyl absorption in the IR at 1775 cm^{-1} which is in the range for a cyclobutenone. However, the ^{1}H NMR indicated that this compound was likely a dimer, and in ether case would be less than 5% yield. A fourth fraction (R_f = 0.13) was collected which was not pure but assuming that it was and that it had the same molecular weight as **17d** would be less than 5% yield. The fifth band to elute (R_f > 0.1) was the second major product which was identified as the α-hydroxylated quinone **63d** (5%) on the basis of the following spectral data: ^{1}H NMR: δ 1.06 (t, 3H, J 7.4 Hz), 1.75 (m, 1H), 1.89 (m, 1H), 2.33 (d, 1H, J 5.8 Hz), 4.78 (m, 1H), 6.99 (s, 1H), 7.75 (m, 2H), 8.10 (m, 2H); IR (neat): 3200–3600m, 2970m, 2940m, 2860w, 1665s, 1620m, 1595m, 1300m cm^{-1}; mass spectrum m/e (% relative intensity) 217 (10), 216 M^+ (60), 187 (100), 159 (32), 102 (19), 77 (23).

The crude residue from the reaction in acetonitrile was also oxidized by CAN in THF and the mixture of products obtained was chromatographed on silica gel to give the quinone **17d** as the major product in 45% yield. A number of small fractions were obtained which were screened by IR in an attempt to determine if cyclobutenone **16d** was formed in this reaction. One fraction ($R_f = 0.22$, 1/1/15) revealed a carbonyl stretch between 1750–1769 cm^{-1} and upon purification it was found that this component was the lactone **20d** in 2% yield which gave the following spectral data: ^1H NMR: δ 0.95 (t, 3H, J 7.4 Hz), 1.60 (q, 2H, J 7.4 Hz), 2.29 (m, 2H), 3.33 (s, 3H), 6.90 (t, 1H, J 1.6 Hz), 7.40 (m, 3H), 7.48 (m, 2H); IR (neat): 2970m, 2940m, 2880m, 1762s, 1450m, 1265m, 1212m, 968m, 902s, 725s cm^{-1}; mass spectrum m/e (% relative intensity) 233 (10), M^+ 232 (65), 204 (34), 202 (33), 201 (100), 190 (19), 173 (73), 159 (42), 155 (34), 145 (30), 115 (33), 105 (78), 91 (26), 77 (88).

The crude mixture from the reaction in acetonitrile was also directly oxidized with CAN in acetonitrile to give two products that were isolated by silica gel chromatography. The first band to elute was the quinone **17d** ($R_f = 0.20$, 1/1/10) which was obtained in 53% yield. The second band to elute ($R_f = 0.04$, 1/1/10) was identified as the quinone mono-acetal **62** which was obtained in 45% yield and characterized by the following spectral data: ^1H NMR (CD_2Cl_2): δ 0.95 (t, 3H, J 7.3 Hz), 1.13 (t, 3H, J 7.3 Hz), 1.27–1.34 (m, 1H), 1.34–1.43 (m, 1H), 1.60–1.68 (m, 1H), 1.70–1.77 (m, 1H), 1.79–1.88 (m, 1H), 2.02–2.08 (m, 1H), 2.42–2.48 (m, 1H), 2.52–2.58 (m, 1H), 3.90–3.96 (m, 1H), 4.23 (d, 1H, J 10.2 Hz), 6.14 (s, 1H), 7.23–7.33 (m, 5H), 7.39 (t, 1H, J 8 Hz), 7.52 (t, 1H, J 7.5 Hz), 7.57 (t, 1H, J 7.5 Hz), 7.64 (d, 1H, J 8 Hz); IR (neat): 3180w, 2975m, 2945m, 2885m, 1780s, 1675s, 1600m, 1460m, 1310m, 1240m, 1185m, 983m, 765m, 690m cm^{-1}; mass spectrum: m/e (% relative intensity) 402 M^+ (4), 203 (20), 202 (92), 173 (18), 160 (89), 159 (74), 120 (25), 105 (100), 77 (53).

A non-oxidative workup was also employed for the reaction in acetonitrile in an effort to identify cyclobutenone products from this reaction which may be destroyed by CAN. The crude reaction residue was dissolved in THF and placed in a bomb which was pressurized to 600 psi with carbon monoxide. After 36 h the solution was removed from the bomb, decanted, concentrated, and chromatographed on silica gel. Two main fractions were collected. The most polar ($R_f = 0.23$, 1/1/15) was found to be the naphthol **65d** which was obtained in 48% yield; ^1H NMR: δ 1.06 (t, 3H, J 7.3 Hz), 1.75 (sext, 2H, J 7.6 Hz), 2.75 (t, 2H, J 7.4 Hz), 3.98 (s, 3H), 4.72 (s, 1H), 6.60 (s, 1H), 7.46 (t, 1H, J 7.0 Hz), 7.51 (t, 1H, J 7.1 Hz), 8.07 (d, 1H, J 8.3 Hz), 8.19 (d, 1H, J 8.2 Hz). The faster moving fraction ($R_f = 0.33$, 1/1/15) was collected and identified as the ketene trapping product **64d** (31%) on the basis of the following spectral data: ^1H NMR: δ 0.98 (t, 3H, J 7.3 Hz), 1.09 (t, 3H, J 7.3 Hz), 1.53–1.67 (m, 2H), 1.67–1.75 (m, 2H), 1.83–1.90 (m, 1H), 2.08–2.17 (m, 1H), 2.64 (t, 2H, J 7.7 Hz), 3.65 (s, 3H), 4.01 (s, 3H), 4.20 (q, 1H, J 7.7 Hz), 5.48 (d, 1H, J 9.7 Hz), 6.67 (s, 1H), 7.34–7.50 (m, 5H), 7.56 (d, 2H, J 7.1 Hz), 7.72 (d, 1H, J 8.2 Hz), 8.20 (d, 1H, J 8 Hz); IR (neat): 3075w, 2965m, 2940m, 2880m, 1755s, 1640m, 1600m, 1460s, 1380s, 1120s, 770m, 735m, 695m cm^{-1}; mass spectrum: m/e (% relative intensity) 433 (23), M^+ 432 (72), 217 (77), 216 (100), 203 (40), 201 (59), 190 (95), 189 (100), 187 (74), 147 (84), 129 (68), 116 (65), 91 (38). The ^1H NMR of the reaction mixture before separation revealed in addition to the naphthol **63d** and the ketene trapping product **64d** a few other small absorptions in the methoxyl region

and if any were from the cyclobutenone **16d** it would be present in less than 5% yield. The largest of the minor methoxyl absorptions taken together with other absorptions in the crude NMR is most consistent with the indene **12d**.

The stereochemistry of the double bonds in **64d** and **62** was assigned on the basis of the chemical shift of the vinyl hydrogens and their correlation with the shifts of the vinyl hydrogens of known *cis*- and *trans*-isomers of related ketene trapping products [30e]. Oxidation of the ketene trapping product **64d** with CAN in THF gave the quinone **17d** in 15% yield and the quinone mono-acetal **62** in 31% yield and none of the lactone **20d**.

The reaction of the phenylcarbene complex 9 with phenylacetylene

The reaction of the phenyl complex **9** and phenylacetylene was carried out in THF and hexanes according to the general procedure. Several products were observed for both reactions after the normal oxidative workup (CAN). The reaction in THF was complete in 23 h whereas the reaction in hexane required 60 h. In each reaction the major product was the quinone **17e** which was isolated by flash chromatography on silica gel with a 1/1/10 solvent mixture in 67% yield from the THF reaction and in 57% yield from the hexane reaction; **17e**: m.p. 110–112°C (MeOH) (lit. [37] m.p. 110°C); ^{1}H NMR: δ 7.08 (s, 1H), 7.49 (brs, 3H), 7.78 (m, 2H), 7.80 (m, 2H), 8.13 (m, 1H), 8.19 (m, 1H). Three other minor components were isolated from the reaction in THF (weight percentage, 3, 3 and 12%) and also from the reaction in hexane (weight percentage), < 15% each) but these were not further purified or characterized.

The reaction of the phenyl complex 9 with 4,4-dimethyl-2-pentyne

The reaction of complex **9** with 4,4-dimethyl-2-pentyne in hexane was carried out on the same scale and with the same conditions as described in the general procedure. After oxidative workup with CAN, purification on silica gel with a 1/1/10 solvent mixture provided three fractions. The first fraction appeared by ^{1}H NMR to contain several isomeric indenes (11%) that could not be separated and were not further characterized. The second fraction ($R_f = 0.35$) contained one compound which was identified as the quinone **17f**: 32%, yellow oil; ^{1}H NMR: δ 1.46 (s, 9H), 2.31 (s, 3H), 7.61–7.63 (m, 2H), 7.88 (dd, 1H, *J* 1.9, 8.6 Hz), 7.97 (dd, 1H, *J* 1.9, 6.7 Hz): IR (neat): 1665s, 1660s, 1570s, 1285m cm^{-1}; mass spectrum: *m/e* (% rel intensity) 228 M^+ (100), 213 (50), 199 (37), 181 (41), 169 (45), 131 (50), 129 (60), 105 (66). Calcd. for $C_{15}H_{16}O_2$ *m/e* 228.1158; measured 228.1155. The third fraction ($R_f = 0.21$) also contained one compound which was identified as the cyclobutenone **16f**: 10%, white solid, m.p. 66–68°C; ^{1}H NMR: δ 1.05 (s, 9H) 2.45 (s, 3H), 3.28 (s, 3H), 7.35 (t, 1H, *J* 7.4 Hz), 7.41 (t, 2H, *J* 7.2 Hz), 7.73 (d, 2H, *J* 7.3 Hz); ^{13}C NMR (100 MHz): δ 14.74, 26.52, 36.06, 52.76, 105.04, 127.69, 128.77, 129.02, 129.14, 147.76, 175.54, 194.79; IR ($CDCl_3$): 3060m, 1750s, 1630s, 1595s, 1208s, 1120m; mass spectrum: *m/e* (% relative intensity) 244 M^+ (33), 229 (40), 210 (70), 187 (100), 159 (57), 115 (30). Calcd. for $C_{16}H_{20}O_2$ *m/e* 244.1465; measured 244.1464. If the oxidative workup of the crude reaction mixture was effected with excess $FeCl_3$-DMF complex in THF instead of aqueous CAN then a 23% yield of the cyclobutenone **16f** was obtained. The cyclobutenone **16f** appeared to be a single isomer by ^{1}H NMR; a GC spectrum of **16f** (1/4″ × 10′ 15% OV-1701 on Chromosorb W, 160°C, 14.38 min) revealed the presence of two minor components both less than 5%.

The same reaction run in THF solvent under the same conditions gave a 14% yield of the cyclobutenone **16f** and a 26% yield of the quinone **17f** after oxidative workup with ferric chloride-DMF complex. This reaction has been reported in t-butyl methyl ether to give a 59% yield of a 92/8 mixture of isomeric naphtholylchromium tricarbonyl complexes from which **17f** is derived [4b]. We have not determined the source of the discrepancy between these experiments. The reaction of complex **9** and 4,4-dimethyl-2-pentyne in acetonitrile gave a 27% yield of the cyclobutenone **16f** and a small amount of a white solid (9%) that had an R_f value and a ^{1}H NMR spectrum identical to those of an authentic sample of biphenyl.

The reaction of the o-methoxyphenylcarbene complex 5 with dimethylacetylene

This reaction was investigated in both THF and acetonitrile. Following the general procedure, this reaction was complete in acetonitrile in 19 h at 45 °C and oxidation was affected by stirring in air for 5 h. After the usual workup, the crude reaction mixture was flash chromatographed on silica gel with a 1/1/6 solvent mixture to provide four fractions. Fraction 1, R_f (1/1/10) = 0.35, was tentatively identified as the indene **18g** and was obtained as a white solid in 11% yield: ^{1}H NMR: δ 1.92 (s, 3H), 1.97 (s, 3H), 3.02 (s, 3H), 4.93 (s, 1H), 6.70 (d, 1H, *J* 8.3 Hz), 6.76 (d, 1H, *J* 7.3 Hz), 7.24 (t, 1H, *J* 7.7 Hz), 7.24 (t, 1H, *J* 7.7 Hz); IR ($CDCl_3$) 1640s, 1582m, 1480s, 1360s cm^{-1}. Fraction 2, R_f (1/1/6) = 0.28–0.30, contained a chromium impurity and was repurified by oxidation with CAN and then preparative TLC to give a colorless oil that was tentatively identified as the indene **12g** in about 9% yield: ^{1}H NMR: δ 1.24 (d, 3H, *J* 7.5 Hz), 1.92 (s, 3H), 3.09 (q, 1H, *J* 7.4 Hz), 3.78 (s, 3H), 3.87 (s, 3H), 6.77 (d, 1H, *J* 8.1 Hz), 6.95 (d, 1H, *J* 7.3 Hz), 7.09 (t, 1H, *J* 7.7 Hz); IR ($CDCl_3$): 1640s, 1585m, 1480s, 1360s cm^{-1}. Fraction 3 was identified as the cyclobutenone **16g** and was obtained in 30% yield as a pale yellow oil, R_f (1/1/6) = 0.1: ^{1}H NMR: δ 1.78 (s, 3H), 2.05 (s, 3H), 3.37 (s, 3H), 3.76 (s, 3H), 6.87 (d, 1H, *J* 8.2 Hz), 6.96 (t, 1H, *J* 7.4 Hz), 7.26 (dt, 1H, *J* 2.2, 7.2 Hz), 7.56 (dd, 1H, *J* 1.5, 7.7 Hz); IR ($CDCl_3$): 1758s, 1635s, 1465s, 1380m cm^{-1}; mass spectrum: *m/e* (% relative intensity) 232 M^+ (23), 217 (30), 189 (22), 135 (100), 92 (19), 77 (30). Calcd. for $C_{14}H_{16}O_3$ *m/e* 232.1099, measured 232.1089. The most polar fraction was purified by preparative TLC using EtOAC/hexanes (2/8), R_f = 0.13, to give the quinone **17g** in 3% yield as a yellow solid: m.p. 146–146.5 °C (MeOH) (lit. [38] m.p. 146–147 °C), ^{1}H NMR: δ 2.11 (s, 3H), 2.13 (s, 3H), 3.98 (s, 3H), 7.22 (d, 1H, *J* 7.0 Hz), 7.59 (t, 1H, *J* 8.3 Hz), 7.71 (d, 1H, *J* 7.0 Hz), mass spectrum: *m/e* (% relative intensity) 216 M^+ (84), 201 (24), 187 (25), 174 (33), 145 (33), 115 (48), 104 (37), 91 (30), 76 (100), 42 (63), 39 (40).

The reaction of complex **5** with 2-butyne in THF was carried out in a similar manner and gave the quinone **17g** in 68% yield after oxidative workup with CAN as the only compound that was observed to elute from the silica column.

The reaction of the o-methoxyphenylcarbene complex 5 with 1-pentyne

This reaction was investigated in THF, CH_3CN, hexane, benzene and CH_2Cl_2 and all were carried out on the same scale and under the same conditions (45 °C for 24 h, except for CH_2Cl_2 which was run at 55 °C for 30 h). The oxidative workup for each reaction employed CAN. The only product isolated in each case was the quinone **17h** which was purified from each reaction mixture by flash elution through silica gel with a 1/1/4 solvent mixture. **17h**: yellow solid, m.p. 64–65 °C

(MeOH/H_2O) (lit. [39] m.p. 64°C), ^{1}H NMR: δ 0.99 (t, 3H, J 7.4 Hz), 1.60 (m, 2H), 2.49 (t, 2H, J 8.2 Hz), 4.00 (s, 3H), 6.68 (s, 1H), 7.28 (d, 1H, J 8.4 Hz), 7.65 (t, 1H, J 8.2 Hz), 7.75 (d, 1H, J 7.6 Hz); IR (CCl_4): 1660s, 1630w, 1590m, 1475m, 1290s, 1262s cm^{-1}. The yields of **17h** for each solvent are listed in Table 2. The reaction in CH_2Cl_2 was the only one that was not clean by TLC. Trace amounts of other compounds were mobile on TLC but in too small quantities to conveniently isolate and identify. The yield of **17h** from the acetonitrile reaction varied somewhat (57–69%) which was suspected to be dependent on the oxidation time with CAN (10–45 min).

If an oxidative workup with CAN is not employed for the reaction in acetonitrile, but rather the crude reaction residue is treated with 650 psi of CO in THF at 25°C for 26 h then chromatographic separation gives two compounds. The first was identified as the naphthol **65h** which was quantified and confirmed by oxidation with CAN to the quinone **17h** (57%). The second compound was tentatively identified as the ketene trapping product **64h** (18–23%) on the basis of its ^{1}H NMR spectrum: δ 0.96 (t, 3H, J 7.4 Hz), 1.04 (t, 3H, J 7.3 Hz), 1.50–1.85 (m, 6H), 2.63 (t, 2H, J 7 Hz), 3.48 (s, 3H), 3.87 (s, 3H), 3.96 (s, 6H), 4.20 (m, 1H), 5.15 (d, 1H, J 9 Hz), 6.70 (s, 1H), 6.82 (d, 1H), 6.95–7.05 (m, 2H), 7.3–7.5 (m, 4H). The stereochemistry of the enol ether of **64h** was assigned on the basis of the chemical shift of the vinyl hydrogen and on the known chemical shifts for the vinyl hydrogens of both the *cis* and *trans* isomers of known related ketene trapping products [30f]. No evidence could be found for the presence of cyclobutenones from this reaction.

*The reaction of the dimethylaminocarbene complex **46** with diethylacetylene*

A solution of 1.00 g (3.07 mmol), of complex **46** [40] and 0.72 g (8.8 mmol), of 3-hexyne in 30 ml of THF was deoxygenated by the freeze-thaw method (−196 0°C, 3 cycles), and sealed in a thick-walled Carius tube and heated in an oil bath at 115°C for 5 d. The contents of the tube were cooled to 25°C, opened to the air, filtered through celite and evaporated to dryness. One-fourth of the crude reaction mixture was eluted on a 20 × 20 cm 2000 μ preparative silica gel plate with a 1/1/4 solvent mixture and a single development gave separation of the three major components. The fastest moving band (R_f = 0.42) was isolated (0.0322 g, 0.71 mmol, total yield 22%), and identified as a single isomer of the indanone **48** on the bais of the following ^{1}H NMR: δ 0.96 (t, 3H, J 7.3 Hz), 1.00 (t, 3H, J 7.1 Hz), 1.63–1.75 (m, 2H), 1.82–1.95 (m, 2H), 2.31 (m, 1H), 3.03 (m, 1H), 7.35 (t, 1H, J 7.5 Hz), 7.46 (d, 1H, J 7.7 Hz), 7.58 (t, 1H, J 8.0 Hz), 7.71 (d, 1H, J 7.7 Hz). The assignment was confirmed when the indenyl ether **12a** (prepared from the reaction of diethylacetylene and the tungsten complex corresponding to **9** [22]), was subjected to acid hydrolysis (10% HCl/ether, 25°C, 12 h) and was cleanly converted to a single compound that had a ^{1}H NMR spectrum, and R_f value (0.42, co-spotted), and retention time on GC (0.25″ × 6′, 5% FFAP on Chromosorb W, 180°C, 5.4 min), identical to that obtained for the indanone **48** isolated from this reaction. The second fraction was isolated (0.052 g, 0.239 mmol, total yield 31%), and identified as the amino indene **47** on the basis of the following spectral data: ^{1}H NMR: δ 1.13 (m, 6H), 2.31 (s, 6H), 2.48 (m, 4H), 4.19 (s, 1H), 7.03 (d, 1H, J 8 Hz), 7.16 (d, 1H, J 7 Hz), 7.22 (m, 2H); IR ($CHCl_3$): 2960m, 2925m, 2875m, 1605m, 1455m, 1415m, 1020w, 905s cm^{-1}; mass spectrum: m/e (% relative intensity) 215 M^+ (10), 200 (10), 187 (13), 186 (100), 171 (16), 170 (17), 160 (26), 155 (23), 145 (23), 143 (28), 141

(34), 128 (35), 91 (21), 77 (10). This product underwent hydrolysis (3 *N* HCl in ether) to give a compound that had a ^{1}H NMR spectrum, an R_f value, and a GC retention time identical to those for indanone **48**. The third fraction ($R_f = 0.09$), was isolated (0.0245 g, 0.107 mmol, total yield 14%), and identified as the lactam **49** on the basis of the following spectral data: ^{1}H NMR: δ 0.94 (t, 3H, *J* 8 Hz), 1.13 (t, 3H, *J* 8 Hz), 1.90 (m, 2H), 2.33 (m, 2H), 2.77 (s, 3H), 4.69 (s, 1H), 7.08 (d, 2H, *J* 7 Hz), 7.33 (m, 3H); IR ($CHCl_3$): 2975s, 2945m, 2900w, 2885w, 1675s, 1505m, 1415s, 1400s, 1025m, 920w cm^{-1}; mass spectrum: *m/e* (% relative intensity) 230 (8), 229 M^+ (37), 214 (35), 200 (100), 186 (7), 172 (15), 157 (9), 152 (12), 129 (12), 128 (12), 118 (43), 115 (18), 91 (45), 77 (23), 42 (28). Calcd. for $C_{15}H_{19}NO$ *m/e* 229.1449, measured 229.1449.

When a portion of the crude reaction mixture was oxidized with CAN according to the general procedure, the quinone **17c** could not be detected in the crude reaction mixture by ^{1}H NMR (500 MHz) or by TLC.

When this reaction was carried out in toluene rather than THF employing the same procedure and scale as described above, the results were similar: **47**, 22%; 48, 14%, **49**, 22%. The reaction in THF at 95 °C for 2.5 d gave **47** in 13%, **48** in 46% and **49** in 15% yield, whereas, the reaction in toluene at 95 °C for 2.5 d gave **47** in 2%, **48** in 2% and **49** in 19% yield.

The photochemical reaction of the o-methoxyphenylcarbene complex 5 with diethylacetylene

In a water cooled photochemical reactor fitted with a vycor filter and 450 watt Hanovia lamp was placed 1.000 g (2.92 mmol) of the carbene complex **5**, 150 ml of anhydrous THF, and a magnetic stirbar. Subsequently, the reactor was flushed with argon for 10 min while the mixture was stirred. Diethylacetylene, 0.36 g (4.4 mmol, 0.33 ml) was then added via the sample port, and the mixture irradiated for 2 h 15 min at 15 °C with stirring and a slight positive pressure of argon maintained within the vessel. When TLC indicated the reaction was completed (disappearance of **5**) the reactor was opened and the contents stirred in air for 2 h at room temperature. Chromium(III) salts were then removed by filtering the crude products first through a Buchner tunnel, and then through silica gel with ether as eluent. TLC of the crude reaction mixture revealed the presence of five components: $R_f = 0.27$, 0.42, 0.50, 0.61, and 0.74 (with a 1/1/4 mixture of ether, methylene chloride and hexane). After removal of solvents, the reaction products were separated by preparative gas chromatography (145 °C, 8′ × 1/4″ 5% FFAP on Chromosorb W), and the five products with the greatest peak areas were collected. All yields were determined by GC with bibenzyl as the internal standard. Response factors of the minor products were assumed to be equal to that of the major product **18a**. Oxidation of a small portion of the crude reaction mixture with CAN and development upon TLC indicated the absence of 5-methoxy-2,3-diethyl-1,4-naphthoquinone (**17a**) by co-spotting with an authentic sample. The spectral data for the five major products from the reaction are given below.

1,7-Dimethoxy-2,3-diethylindene (**18a**). Identification was made on the basis that its GC retention time, ^{1}H NMR and mass spectra were identical to those of the compound isolated from the reaction of complex **5** and diethylacetylene in acetonitrile. Yield 49.3%.

7-Methoxy-2,3-diethylindanone (**54**). (After isolation by GC the product was

purified by preparative TLC on a 250 μ silica gel plate): ^{1}H NMR: δ 0.93 (t, 3H, J 7.6 Hz), 0.99 (t, 3H, J 7.5 Hz), 1.63 (m, 2H), 1.85 (m, 2H), 2.26 (m, 1H), 2.95 (m, 1H), 3.93 (s, 3H), 6.76 (d, 1H, J 8.1 Hz), 7.00 (d, 1H, J 7.5 Hz), 7.50 (m 1H): IR ($CHCl_3$): 2970w, 2940w, 1700s, 1600m, 1480w, 1110m, 910s cm^{-2}; mass spectrum: m/e (% relative intensity) 218 M^+ (23), 190 (100), 189 (42), 175 (57), 161 (59), 154 (11), 143 (8), 128 (12), 115 (20), 103 (10), 91 (15), 77 (13); calcd. for $C_{12}H_{18}O_2$ m/e 218.1307; measured 218.1318. Yield 4%.

7-Methoxy-2,3-diethylindene (**53**). ^{1}H NMR: δ 1.13 (t, 3H, J 7.6 Hz), 1.15 (t, 3H, J 7.2 Hz), 2.47 (q, 2H, J 7.5 Hz), 2.51 (q, 2H, J 7.6 Hz), 3.23 (s, 2H), 3.88 (s, 3H), 6.67 (d, 1H, J 8.1 Hz), 6.92 (d, 1H, J 7.5 Hz), 7.23 (t, 1H); IR ($CHCl_3$): 2960s, 2930m, 2870w, 1610s, 1580s, 1475m, 1460m, 1355s, 1060m cm^{-1}; mass spectrum: m/e (% relative intensity) 202 M^+ (44), 158(45), 143(32), 141(32), 128 (72), 115 (100); calcd. for $C_{14}H_{18}O$ m/e 202.1359; measured 202.1368. Yield 5.3%.

4-Methoxy-1,2-diethylindene (**52**) (additionally purified by preparative TLC on a 250 μ silica gel plate): ^{1}H NMR: δ 0.54 (t, 3H, J 7.5 Hz), 1.25 (t, 3H, J 7.6 Hz), 1.59 (m, 1H), 1.82 (m, 1H), 2.32 (m, 2H), 3.37 (m, 1H), 3.87 (s, 3H), 6.63 (s, 1H), 6.75 (d, 1H, J 7.8 Hz), 6.98 (d, 1H, J 7.3 Hz), 7.08 (t, 1H); IR ($CHCl_3$): 2970m, 2940m, 2880w, 2840w, 1580m, 1480m, 1265s cm^{-1}; mass spectrum: m/e (% relative intensity) 202 M^+ (5), 169 (42), 154 (100), 153 (38), 152 (26), 128 (6), 115 (7), 128 (6), 115 (7), 105 (8), 100 (11), 91 (10), 77 (12); calcd. for $C_{14}H_{18}O$ m/e 202.1359; measured 202.1368. Yield 2.1%.

Methyl(*o*-methoxy)benzoate (**55**). The ^{1}H NMR, mass spectrum and retention time on GC were found to be identical to those of an authentic sample; yield 2.0%.

The photochemical reaction of the phenylcarbene complex 9 with diethylacetylene and diphenylacetylene

In a standard water cooled (8° C) photochemical reactor fitted with a vycor filter and a 450 watt Hanovia Hg low pressure lamp was placed 0.1000 g (0.3203 mmol) of the carbene complex **9**, 170 ml of anhydrous THF, and a magnetic stirbar. After flushing the mixture with argon for 10 min 0.0936 g (1.14 mmol, 0.13 ml) of 3-hexyne was added via the addition port. After the reactants were thoroughly mixed the lamp was ignited and the photoysis continued for 30 min, with maintenance of a slight positive pressure of argon and a vigorous stirring rate. The temperature of the reaction solution reached a maximum of 15° C. Subsequently, the reactor was opened and the mixture oxidized with a 0.5 M solution of aqueous ceric ammonium nitrate, and then stirred for 30 min. Separation of the THF layer, drying the solution over $MgSO_4$, removal of solvent, and column chromatography upon silica gel (1/1/10 Et_2O/CH_2Cl_2/hexanes) gave 0.0372 g (1.74 mmol) of **17c** in 54.2% yield. The ^{1}H NMR and mass spectrum and R_f value on TLC were found to be identical to those of an authentic sample. No attempts were made to find and identify any minor products from this reaction. When the reaction was repeated in an identical manner and methanol was substituted for THF as the solvent, the isolated yield of **17c** was 32%.

In the same manner as above 1.00 g (3.203 mmmol) of **9** and 0.571 g (3.20 mmol) of diphenylacetylene gave after identical conditions of photolysis and workup, two products: quinone **17b**, 0.363 g (1.17 mmol, 36.5%), and 0.0262 g (0.093 mmol, 2.9%) of indenone **19b**. Both products were found to have ^{1}H NMR and mass spectra that were identical to those of authentic samples.

Photolysis of **9** in the presence of diethylacetylene at −78°C: In a dry 80 ml quartz test tube was placed 0.1057 g (0.339 mmol) of carbene complex **9**, 18 ml of anhydrous THF, and a magnetic stirbar. After flushing with argon for 10 min, the tube was immediately sealed with a rubber septum and 0.097 g (1.18 mmol, 0.13 ml) of 3-hexyne was then added by syringe. The mixture was stirred briefly and placed in a hexane dry ice bath contained within a silvered Dewar which had a 1″ × 6″ window. The mixture was subsequently photolyzed for 13.5 h with a 450 watt Hanovia lamp placed in a water-cooled quartz jacket flush to the window of the Dewar. The mixture was then oxidized at −78°C with slow dropwise addition of 10 ml of 0.5 *M* aqueous ceric ammonium nitrate with vigorous mixing after each addition. The usual workup by silica gel column chromatography afforded 0.0320 g (0.149 mmol) of **17c** in 44.1% yield.

The synthesis of the o-t-butyloxyphenylchromium carbene complex ***56***

t-Butyl phenyl ether was prepared according to the literature procedure: b.p. 58–63°C/5 mmHg [41]; ^{1}H NMR: δ 1.34 (s, 9H), 6.97 (d, 2H, *J* 7.5 Hz), 7.04 (t, 1H, *J* 7.3 Hz), 7.23 (t, 2H, *J* 7.8 Hz). A solution of t-butylphenyl ether (1.5 g, 10 mmol) in ether (10 ml) was deoxygenated by the freeze-thaw method (−196°C/0°C, 2 cycles). t-BuLi (5.88 ml, 1.7 *M*, 10 mmol) was then added at room temperature and the solution was stirred for 2 d to generate *ortho*-t-butyloxyphenyllithium [42]. The pink supsension was then transferred by canula into a slurry of $Cr(CO)_6$ (2.2 g, 10 mmol) in ether (30 ml) at 25°C. After stirring for 30 min, the yellow solution was cooled to 0°C and $MeOSO_2F$ (1.6 ml, 20 mmol) was added dropwise. After 1.5 h, aqueous $NaHCO_3$ (10 ml) was added and stirring was continued for 30 min. The orange-yellow solution was extracted with ether, washed with brine and dried ($MgSO_4$). The red residue obtained after evaporation was flash chromatographed on silica gel with hexanes to give **56** as a solid, $R_f = 0.36$ (1.45 g, 3.9 mmol, 39%): m.p. 79.5–81°C; ^{1}H NMR: δ 1.49 (s, 9H), 3.9–4.4 (brs, 3H), 6.85 (dd, 1H, *J* 1.7, 7.6 Hz), 6.95 (t, 1H, *J* 7.4 Hz), 7.01 (d, 1H, *J* 8.4 Hz), 7.17 (dt, 1H, *J* 1.6, 8.0 Hz); ^{13}C NMR (100 MHz): δ 28.83 (q, *J* 127.5 Hz), 64.92 (q, *J* 132.1 Hz), 79.10 (dectet, *J* 3.4 Hz), 115.60 (d, *J* 119.9 Hz), 100.03 (d, *J* 160.8 Hz), 123 (d, *J* 158.0 Hz), 129.0 (d, *J* 157.7 Hz), 142.28, 145.26, 216.28, 225.03, 355.2; IR (CH_2Cl_2): 2065s, 1984s, 1919s, 1580m, 1113m, 1046m cm^{-1}; mass spectrum: *m/e* (% relative intensity) 328 M^+ (12) 300 (12), 272 (23), 244 (45), 220 (18), 188 (63), 158 (100), 144 (46), 120 (56), 108 (30), 92 (18), 80 (53); calcd for $C_{17}H_{16}O_7Cr$ *m/e* 384.0301; measured 384.0311.

The reaction of the o-t-butyloxyphenylcarbene complex ***56*** *with 3-hexyne in THF*

This reaction was carried out on the same scale and under the same conditions as described in the general procedure. After the usual hydrolytic and oxidative (CAN) workup the crude reaction mixture was flash chromatographed on silica gel with a 1/1/20 solvent mixture to provide two fractions. Fraction 1, R_f (1/1/10) = 0.13, was identified as the indene **18k** and obtained as an oil in 4% yield: ^{1}H NMR: δ 1.14 (t, 6H, *J* 7.7 Hz), 1.46 (s, 9H), 2.24–2.30 (m, 1H), 2.42–2.46 (m, 2H), 2.59–2.61 (m, 1H), 3.05 (s, 3H), 5.06 (s, 1H), 6.80 (d, 1H, *J* 8.5 Hz), 6.83 (d, 1H, *J* 7.3 Hz), 7.15 (t, 1H, *J* 7.7 Hz); IR ($CDCl_3$): 2965s, 2934s, 2875s, 1660m, 1586s, 1379s, 1261s, 1240s, 1184s, 1131m, 1036 cm^{-1}; mass spectrum: *m/e* 274 M^+ (15), 230 (17), 218 (40), 202 (17), 189 (100), 174 (13), 161 (13), 145 (14), 128 (13), 115 (17).

Fraction 2 R_f (1/1/10) = 0.12, was identified as the quinone **17k** and was obtained as a yellow oil in 72% yield: ^{1}H NMR δ 1.14 (t, 6H, *J* 7.5 Hz), 1.46 (s, 9H), 2.61 (q, 2H, *J* 7.4 Hz), 2.62 (q, 2H, *J* 7.4 Hz), 7.34 (d, 1H, *J* 8.1 Hz), 7.50 (t, 1H, *J* 7.9 Hz), 7.80 (t, 1H, *J* 7.0 Hz); ^{13}C NMR (100 MHz): δ 13.76 (tq, *J* 3.9, 140.0 Hz), 13.97 (tq, *J* 4.9, 129.3 Hz), 19.88 (tq, *J* 3.9, 140.0 Hz), 20.22 (tq, *J* 4.1, 135.0 Hz), 28.81 (q of quintet, *J* 4.1, 126.0 Hz), 81.76 (dectet, *J* 4.2 Hz), 121.35 (dd, *J* 7.0, 162.2 Hz), 132.90 (d, *J* 162.6 Hz), 134.42 (d, *J* 7.8 Hz), 145.57 (m), 149.80 (m), 155.84 (d, *J* 9.3 Hz), 184.28 (t, *J* 4.7 Hz), 185.12 (q, *J* 4.0 Hz); mass spectrum: *m/e* (% relative intensity) 286 M^+ (2), 230 (100), 215 (83), 187 (13), 120 (15), 92 (11); calcd for $C_{14}H_{14}O_3$ *m/e* 230.0943; measured 230.0948.

When the reaction mixture was air oxidized and chromatographed a small fraction was obtained (< 2% by weight) that by ^{1}H NMR was judged to contain some of the indene **12k**.

*Reaction of the o-t-butyloxyphenylcarbene complex **56** with 3-hexyne in CH_3CN*

The reaction was carried out according to the general procedure except that the crude reaction mixture was oxidized with a solution of excess $FeCl_3$-DMF in THF. After the normal workup, the products were separated by flash chromatography on silica gel with a 1/1/2 solvent mixture. Fraction 1, R_f (1/1/20) = 0.35 was identified as the indene **12k** and obtained as a colorless oil in 6% yield: ^{1}H NMR: δ 0.49 (t, 3H, *J* 7.4 Hz), 1.12 (t, 3H, *J* 7.6 Hz), 1.35 (s, 9H), 1.81–1.82 (m, 1H), 1.96–2.04 (m, 1H), 2.06–2.12 (m, 1H), 2.64–2.68 (m, 1H 3.33 (t, 1H, *J* 4.7 Hz),), 3.76 (s, 3H), 6.88 (dd, 1H, *J* 1.2, 7.3 Hz), 7.01–7.06 (m 2H); ^{13}C NMR (100 MHz): δ 7.86 (q, *J* 126.0 Hz), 14.32 (tq, *J* 4.6, 12.70), 17.63 (qt, *J* 5.3, 126.2 Hz), 22.50 (t, *J* 128.3 Hz), 28.61 (heptet of q, *J* 5.7, 125.7 Hz), 45.40 (d, *J* 126.0 Hz), 60.71 (q, *J* 144.3 Hz), 79.65 (decet, *J* 3.4 Hz), 118.36 (dd, *J* 8.9, 159.0 Hz), 122.41 (dd, *J* 8.2, 158.4 Hz), 124.85 (d, *J* 160.0 Hz), 133.0 (brs), 134.76 (s); IR ($CDCl_3$): 2964s, 2932s, 2874s, 1629m, 1580m, 1283s, 1236s, 1183s, 1040m cm^{-1}; mass spectrum: *m/e* (% rel intensity) 274 M^+ (37), 218 (85), 203 (28), 189 (100), 174 (17), 115 (13). Fraction 2, R_f (1/1/20) = 0.13, was identified as the indene **18k** (12% yield). The ^{1}H NMR, IR, and mass spectrum of this product were found to be identical to those of the product isolated from the reaction in THF. Fraction 3 was identified as the quinone **17k** (24%) by comparison of its ^{1}H NMR data with that obtained from the THF reaction. Fraction 4 contained chromium(III) species and was further oxidized in air for 2 d. Subsequent purification by flash chromatography (1/1/10), R_f = 0.21, gave a colorless liquid that was identified as the cyclobutenone **16k** (23%) on the basis of the following spectral data: ^{1}H NMR: δ 1.06 (t, 3H, *J* 7.6 Hz), 1.19 (t, 3H, *J* 7.7 Hz), 1.44 (s, 9H), 2.27 (q, 2H, *J* 7.6 Hz), 2.43 (q, 2H, *J* 7.6 Hz), 3.40 (s, 3H), 6.93 (dt, 1H, *J* 1.1, 7.8 Hz), 7.06 (dd, 1H, *J* 1.0, 8.3 Hz), 7.15 (ddd, 1H, *J* 1.8, 7.2, 8.3 Hz), 7.55 (dd, 1H, *J* 1.8, 7.7 Hz); ^{13}C NMR (100 MHz): δ 11.36, 11.93, 17.23, 20.65, 20.11, 53.47, 79.23, 98.09, 117.90, 120.51, 127.35, 128.11, 128.55, 154.08, 154.32, 178.04, 192.32; IR (neat): 2976s, 2937s, 1759s, 1637m, 1596m, 1483s, 1450s, 1368m, 1246m, 1170s, 1090m, 1483s, 1450s, 1368m, 1246m, 1170s, 1090m, 903m cm^{-1}.

*The reaction of the p-methoxyphenylchromiumcarbene complex **57** with diethylacetylene in THF, hexane and acetonitrile*

The reaction of complex **57** [31] and diethylacetylene in THF was carried out according to the general procedure. After (CAN) oxidation of the crude reaction

mixture (reaction complete in 36 h) and the usual workup, the product quinone **17l** ($R_f = 0.37$) was purified by flash chromatography on silica gel with a 1/1/10 solvent mixture and obtained in 85% yield as a yellow solid: m.p. 57 °C; ^{1}H NMR: δ 1.15 (t, 6H, *J* 7.7 Hz), 2.62 (q, 4H, *J* 7.5 Hz), 3.94 (s, 3H), 7.15 (dd, 1H, *J* 2.6, 8.6 Hz), 7.50 (d, 1H, *J* 2.6 Hz), 8.01 (d, 1H, *J* 8.6 Hz); ^{13}C NMR: δ 185.0, 184.0, 163.6, 148.1, 147.4, 134.0, 128.5, 125.7, 119.9, 109.2, 55.7, 20.0, 13.9; IR ($CHCl_3$): 3041m, 2970m, 2930w, 2870w, 2840w, 1655s, 1610w, 1590s, 1575m, 1490w, 1460w, 1305s cm^{-1}; mass spectrum: *m/e* (% relative intensity) 245 (17), 244 M^+ (100), 229 (48), 201 (22), 187 (8), 135 (8), 115 (7), 106 (8), 77 (5), 69 (7); calcd. for $C_{15}H_{16}O_3$ *m/e* 244.1099; measured 244.1089.

The reaction of complex **57** and diethylacetylene in hexane gave an 80% yield of the quinone **17l** under the same conditions. The same reaction in acetonitrile was subjected to an oxidative workup under three separate conditions. Employing the normal oxidative workup with CAN the quinone **17l** was obtained in 44% yield and no products corresponding to the cyclobutenone **16l** eluted from the silica gel column. When the reaction mixture in acetonitrile was oxidized with $FeCl_3$-DMF complex, the quinone **17l** was obtained in 20% yield and also eluting from the column was a fraction containing a mixture of compounds which had peaks in the ^{1}H NMR that were consistent with indene products but were not further separated or characterized. When the crude mixture from the acetonitrile reaction was worked up by exposure to air and chromatographed on silica gel two fractions were obtained in addition to the phenol product. The first fraction by ^{1}H NMR was determined to be a 13/6 mixture of the indenes **12l/18l**. The indene **12l** was obtained in 13% yield after purification by preparative TLC and was characterized by the following spectral data: ^{1}H NMR: δ 0.58 (t, 3H, *J* 7.3 Hz), 1.12 (t, 3H, *J* 7.5 Hz), 1.78 (m, 1H), 2.12 (m, 1H), 2.66 (m, 1H), 3.33 (m, 1H), 3.80 (s, 3H), 3.85 (s, 3H), 6.77 (dd, 1H, *J* 2.2, 8.2 Hz), 6.92 (d, 1H, *J* 2.2 Hz), 7.14 (d, 1H, *J* 8.2 Hz); mass spectrum: *m/e* (% relative intensity) 232 M^+ (38), 217 (38), 203 (100), 188 (30), 173 (10), 159 (6), 145 (8), 128 (6), 115 (8), 91 (6), 85 (96). The second fraction was also repurified by preparative TLC to give the cyclobutenone **16l** in 4% yield and for which the following spectral data were collected: ^{1}H NMR: δ 1.50 (m, 6H), 2.63 (m, 2H), 2.86 (m, 2H), 3.72 (s, 3H), 4.11 (s, 3H), 7.18 (d, 2H, *J* 9 Hz), 7.61 (d, 2H, *J* 9 Hz); ^{13}C NMR: δ 11.1, 12.1, 17.0, 20.8, 53.2, 55.2, 99.9, 113.6, 113.7, 129.94, 155.25, 158.96, 180.6, 193.7; IR ($CDCl_3$): 2938w, 2900w, 1753s, 1712w, 1511m, 1464w, 1176w, 1097w, 1034w, 910w, 835w cm^{-1}; mass spectrum: *m/e* (% relative intensity) 260 M^+(40), 245 (100), 217 (12), 203 (25), 188 (13), 135 (66), 92 (9), 72 (14).

*(1-Cyclohexenylmethoxymethylene)pentacarbonylchromium (71) [43 *]*

Method A. To 7.68 g (20.3 mmol) of cyclohexanone-2,4,6-triisopropyl benzene sulfonyl hydrazone [44] in 50 ml of THF at −78 °C was slowly added by syringe 25.5 ml (39.6 mmol) of a 1.55 *M* solution of n-butyllithium in hexane. The resulting yellow solution was transferred to an ice bath and the solution turned deep red with N_2 evolution. After 15 min the resulting vinyl anion solution was transferred to a slurry of 4.46 g (20.3 mmol) of chromium hexacarbonyl in 50 ml of ether at room temperature. The solution rapidly turned yellow and was stirred for 30 min. To this solution was added 4 ml (50 mmol) of methylfluorosulfonate and the resulting red solution was stirred for 20 min. Powdered Na_2CO_3 was added to destroy the excess

methyl fluorosulfonate. After filtration and dilution with 200 ml of ether, the solution was washed with brine and dried over $MgSO_4$. After removal of solvents, the residue was extracted with several portions of hexane and filtered through celite. The crude reaction mixture was flash chromatographed on silica gel with hexane as solvent to give 3.87 g (12.3 mmol, 62%, $R_f = 0.23$) of **71** as a red oil. ^{1}H NMR: δ 1.58–1.67 (bs, 4H), 2.16 (bs, 2H), 2.32 (bs, 2H), 4.67 (s, 3H), 6.37 (bs, 1H); ^{13}C NMR: δ 21.43, 21.82, 25.25, 25.63, 64.98, 134.98, 154.17, 216.7, 223.8, 350,85; IR (neat): 2920w, 2060s, 1920s, 1620w, 1450m, 1230m, 1122m, 985m, 795 m cm^{-1}; mass spectrum: *m/e* (% relative intensity) 316 M^+ (1.8), 288 (5), 260 (1.7), 232 (1.4), 204 (5), 176 (36), 52 (100). Analysis: $C_{13}H_9O_6Cr$ (C,H,Cr).

Method B. To a solution of 3.0 g (18.6 mmol) of 1-bromocyclohexene [45] in 40 ml of THF at −78°C was added 19.6 ml (37.2 mmol) of a 1.9 *M* solution of t-butyllithium in pentane. After 30 min at −78°C the vinyllithium solution was transferred via canula to a slurry of 4.1 g (18.6 mmol) if $Cr(CO)_6$ in 120 ml of ether at 25°C. After 20 min, the mixture was alkylated by addition of 3.7 ml (46.5 mmol) of $MeSO_3F$. The workup and purification procedure described above gave 3.93 g (12.4 mmol, 67%) of **71**.

(2-Dihydropyranylmethoxymethylene)pentacarbonylchromium (68)

To a solution of 1.68 g (20 mmol) of dihydropyran in 3 ml of THF at −78°C was slowly added 11.2 ml (20 mmol) of a 1.8 *M* solution of t-butyllithium in pentane followed by warming to 0°C and stirring for 30 min. The solution of dihydropyranyllithium [46] was transferred via canula to a slurry of 4.4 g (20 mmol) of $Cr(CO)_6$ in 20 ml of THF at 25°C. After 2 h all volatiles were removed, first on a rotary evaporator and then under high vacuum. The yellow brown solid was extracted into 50 ml of water that had previously been purged with argon and the solution filtered and treated with a solution of 6.45 g of n-Bu_4NBr in 15 ml of H_2O. Filtration gave 9.70 g (82%) of the yellow chromium pentacarbonyl acylate as its ammonium salt which can be stored at 4°C for at least one month.

The ammonium salt (6.0 g, 11.3 mmol) was dissolved in 40 ml of CH_2Cl_2 which had been purged with argon and to this solution was slowly added to 0°C methane fluorosulfonate (0.95 ml, 11.3 mmol). Saturated aqueous $NaHCO_3$ (5 ml) was added after 20 min and the CH_2Cl_2 was removed by evaporation. The residue was extracted with hexane, washed with brine, and dired over $MgSO_4$. The crude mixture was flash chromatographed on silica gel with a 1/1/10 solvent mixture to give 2.72 g of **68** (75%) as red prisms (m.p. 47–48°C); $R_f = 0.52$ (1/1/10), $R_f = 0.08$ (hexane): ^{1}H NMR: δ 1.85 (quintet, 2H), 2.22 (dd, 2H, *J* 6.3, 11.3 Hz), 4.19 (t, 2H, *J* 5.1 Hz), 4.78 (s, 3H), 5.51 (t, 1H, *J* 4.5 Hz); ^{13}C NMR (100 MHz): δ 20.56 (t, *J* 131.0 Hz), 21.32 (t, *J* 134.0 Hz), 66.19 (q, *J* 149.0 Hz), 66.37 (t, $J = 142.3$ Hz), 101.38 (d, *J* 168.3 Hz), 160.58 (s), 216.77 (s), 224.81 (s), 333.84 (s); IR ($CHCl_3$): 2060m, 1980s, 1940s, 1595w, 1230w, 645m, 658m cm^{-1}; mass spectrum: *m/e* (% relative intensity) 318 M^+ (3), 290 (5), 262 (5), 234 (3), 220(2), 206 (16), 178 (85), 52 (100). Analysis: $C_{12}H_{10}O_7Cr$ (C, H, Cr).

Isolation of the acyl metallate as its tetramethylammonium salt gave only a 23% yield due to incomplete precipitation. Methylation of the tetramethylammonium salt by sequential treatment with acetyl chloride and methanol [47] gave only a 36% yield of **68**. Direct methylation of the lithium salt gave an equal mixture of **68** and a second carbene complex ($R_f = 0.14$ (1/1/10)) which was identified as [1-((4-

methoxy)butyloxy)-1-dihydropyranylmethylene]pentacarbonylchromium on the basis of its ^{1}H NMR spectrum; δ 1.83 (m, 4H), 2.08 (m, 2H), 2.22 (q, 2H, J 6.1 Hz), 3.36 (s, 3H), 3.47 (t, 2H, J 6.3 Hz), 4.20 (t, 2H, J 5.0 Hz), 5.09 (t, 2H, J 6.3 Hz), 5.48 (t, 1H, J 4.4 Hz).

*Benzannulation of α,β-unsaturated chromium carbene complexes **68** and **71** with acetylenes in various solvents*

Unless otherwise stated all reactions were carried out under argon in THF ($\sim$ 0.3 M) at 45°C for 24 h with 1.5 equivalents of the acetylene. A typical procedure is given for compound **69a**. The workup of each reaction includes the use of an oxidizing reagent to free the organic moiety (either as a quinone or phenol) from the chromium. In most cases one of the following oxidizing methods was employed. *Method A*; the solution of the crude reaction mixture is stirred vigorously with a 0.5 M ceric ammonium nitrates solution (7.5 equiv.) in 0.1 M aqueous nitric acid at room temperature for 30 min. *Method B*; the solution of the crude reaction mixture was treated with 7.5 equivalents of ferric chloride-DMF complex [10] as a THF solution at 25°C in air for 1 h. In some reactions alternative oxidizing methods are employed and are described where they occur. Only the quinone products (or corresponding phenols) were observed from the reactions of the α,β-unsaturated complexes **64** and **67** with all of the acetylenes and solvents indicated in Tables 5 and 6.

*3,4-Dihydro-2H-1-oxa-7,8-diethyl-5,8-naphthoquinone (**69a**)*

A solution of the dihydropyranyl chromium carbene complex **68** (318 mg, 1.0 mmol) and 3-hexyne (0.17 ml, 1.5 mmol) in 8 ml of THF was degassed by the freeze-thaw method (−196°C/25°C, 3 cycles). The solution was heated under an argon atmosphere at 45°C for 48 h during which time it was monitored by TLC. The reaction mixture was opened to air, combined with 10 ml of a 0.5 M ceric ammonium nitrate solution in 0.1 M aqueous nitric acid and stirred for 30 min at room temperature (method A). The mixture was diluted with ether, washed with water and brine and dried over anhydrous $MgSO_4$. The crude reaction residue was flash chromatographed on silica gel with a 1/1/4 solvent mixture and the quinone **69a** (R_f = 0.25) was obtained as a yellow solid (160 mg, 0.72 mmol, 73%) which was crystallized from methanol (yellow needles, m.p. 107–108°C): ^{1}H NMR: δ 1.08 (t, 6H, J 7.5 Hz), 1.95 (quintet, 2H), 243 (t, 2H, J 6.3 Hz), 2.49 (t, 4H, J 7.5 Hz), 4.23 (t, 2H, J 5.2 Hz); ^{13}C NMR (50 MHz): δ 13.9, 14.2, 17.8, 19.7, 20.7, 67.4, 118.4, 142.8, 145.5, 153.2, 182.1, 186.8; IR ($CHCl_3$): 1660s, 1650s, 1640s, 1610s, 1110s, 910s; mass spectrum: m/e (% relative intensity) 220 M^+ (51), 205 (100), 177 (78), 149 (28), 91 (32), 71 (51), 55 (69), 43 (65). Analysis: $C_{13}H_{16}O_3$ (C, H).

*2,3-Diethyl-5,6,7,8-tetrahydro-1,4-Naphthoquinone (**72a**)*

After workup with oxidation method A the product was purified by flash chromatography on silica gel with a 1/1/12 solvent mixture to give the quinone **72a** in 65% yield (m.p. 78–79°C, R_f = 0.39 (1/1/10)): ^{1}H NMR: δ 1.07 (t, 6H, J 7.5 Hz), 1.67 (brs, 4H), 2.41 (brs, 4H), 2.48 (q, 4H, J 7.5 Hz); IR ($CHCl_3$): 2940m, 2880m, 1645s, 1612m, 1430m, 1295w, 1255w, 960w, 822m cm^{-1}; mass spectrum: m/e (% relative intensity) 218 M^+ (12), 203 (20), 190 (22), 189 (19), 175 (100), 161 (40), 105 (28), 91 (35). Analysis: $C_{14}H_{18}O_2$ (C, H).

2-n-Propyl-5,6,7,8-Tetrahydro-1,4-naphthoquinone (72c)

After workup with oxidation method A the product was purified by flash chromatography ($R_f = 0.34$ (1/1/10)) and obtained in 61% yield as a yellow solid which was crystallized from aqueous methanol to give yellow needles (m.p. 63–64° C): ^{1}H NMR: δ 0.96 (t, 3H, J 7.4 Hz), 1.53 (q, 2H, J 7.5 Hz), 1.69 (s, 4H), 2.34 (t, 2H, J 7.1 Hz), 2.42 (m, 4H), 6.48 (s, 1H); IR ($CHCl_3$): 1645s, 162s, 1392s, 910s cm^{-1}; mass spectrum; *m/e* (% relative intensity) 204 M^+ (100), 189 (52), 176 (62), 161 (55), 147 (50), 91 (48), 79 (62). Analysis: $C_{13}H_{16}O_2$ (C, H).

2-Trimethylsilyl-4-methoxy-5,6,7,8-tetrahydro-1-naphthol (73d)

A deoxygenated solution of 0.1580 g (0.502 mmol) of carbene complex **71** and 0.15 g (1.5 mmol) of trimethylsilylacetylene in 4 ml of THF was heated at 41° C for 8 h under argon. The greenish solution was stirred with an additional 50 ml of THF in air for 4 h. After filtration and removal of solvents the residue was flash chromatographed with a 1/1/40 solvent mixture to give 89.2 mg (0.357 mmol, 71%) of the naphthol **73d** (m.p. 72–73° C, $R_f = 0.34$ (1/1/10)): ^{1}H NMR: δ 0.31 (s, 9H), 1.74–1.83 (m, 4H), 2.55 (t, 2H, J 5.6 Hz), 2.65 (t, 2H, J 6 Hz), 3.79 (s, 3H), 4.42 (s, 1H, exchangable with D_2O), 6.68 (s, 1H); IR ($CHCl_3$): 3605m, 2940s, 1435s, 1390s, 1320s, 1250m, 1090m, 1010m, 840s cm^{-1}; mass spectrum: *m/e* (% relative intensity) 250 M^+ (0.4), 234 (100), 219 (80), 203 (12), 145 (22), 115 (22), 81 (30), 75 (80). Analysis: $C_{14}H_{22}O_2Si$ (C, H).

Also obtained from this reaction was 27.7 mg of an unknown compound ($R_f = 0.58$) which has the following spectral data: ^{1}H NMR: δ 1.43 (s, 9H), 2.27 (s, 2H), 5.01 (s, 1H, exchangable with D_2O), 6.98 (s, 2H); IR ($CHCl_3$): 3640m, 2960s, 2078s, 1430m, 1310w, 1155m cm^{-1}; mass spectrum: *m/e* (% relative intensity) 250 (2), 235 (1), 220 (30), 205 (100), 189 (7), 177 (20), 145 (20), 105 (17), 81 (20), 57 (75).

1-Oxa-2-H-3,4-dihydro-6,7-diethyl-8-methoxy-5-naphthol (70a)

The workup included oxidation by simply stirring open to air for 3 h and then the product was purified by flash chromatography ($R_f = 0.17$ (1/1/4)) and isolated in 80% yield as a colorless oil: ^{1}H NMR: δ 1.40 (m, 6H), 2.05 (m, 2H), 2.58 (q, 2H, J 7.7 Hz), 2.62 (m, 4H), 3.77 (s, 3H), 4.14 (s, 1H), 4.17 (t, 2H, J 5.0 Hz); IR (neat): 3450s, 1615m, 1580m cm^{-1}; mass spectrum: *m/e* (% relative intensity) 236 M^+ (80), 221 (100), 193 (15), 165 (15); calcd. for $C_{14}H_{20}O_3$ *m/e* 236.1412; measured 236.1386.

1-Oxa-2-H-3,4-dihydro-6-n-propyl-5,8-naphthoquinone (69c)

After workup with oxidation method A the product was purified by flash chromatography ($R_f = 0.20$ (1/1/4)) and obtained in 67% yield as a yellow solid (m.p. 62–64° C): ^{1}H NMR: δ 0.97 (t, 3H, J 7.4 Hz), 1.54 (quintet, 2H, J 7.5 Hz), 1.96 (m, 2H), 2.44 (t, 2H, J 6.3 Hz), 2.49 (m, 2H), 4.25 (t, 2H, J 5.2 Hz), 6.49 (s, 1H); IR ($CHCl_3$): 1660s, 1645s, 1608s, 1285s cm^{-1}; mass spectrum: *m/e* (% relative intensity) 206 M^+ (100), 191 (43), 178 (13), 163 (28), 150 (27), 135 (9), 121 (10), 107 (11), 91 (12), 67 (15), 55 (23), 53 (16); calcd. for $C_{12}H_{14}O_3$, *m/e* 206.0943; measured 206.0943.

2,3-Diphenyl-5,6,7,8-tetrahydro-1,4-naphthoquinone (73b)

After workup with oxidation method B the phenol **73b** was isolated in 89% yield as white solid: ^{1}H NMR: δ 1.83 (brs, 4H), 2.74 (m, 2H), 2.83 (brs, 2H), 3.23 (s, 3H),

4.84 (s, 1H), 7.05–7.21 (m, 10H); IR ($CDCl_3$): 3540s, 3030w, 2940s, 1440s, 1255s cm^{-1}; mass spectrum: *m/e* (% relative intensity) 330 M^+ (100), 315 (20), 273 (25), 179 (12); calcd for $C_{23}H_{22}O_2$ *m/e* 330.1229; measured 330.1630.

*1-Oxa-2-H-3,4-dihydro-6,7-diphenyl-8-methoxy-5-naphthol (**70b**)*

The workup involved stirring the hexane solution of the crude reaction mixture with a THF solution of $FeCl_3$-DMF complex (7 equiv.) for 1 h. The product was isolated by flash chromatography on silica gel with a 1/1/4 solvent mixture and obtained as a white solid in 66% yield ($R_f = 0.27$): m.p. 131–132°C (MeOH); ^1H NMR; δ 2.07 (quintet, 2H, *J* 5.2 Hz), 2.78 (t, 2H, *J* 6.3 Hz), 3.46 (s, 3H), 4.29 (t, 2H, *J* 4.9 Hz), 4.90 (s, 1H), 7.04–7.24 (m, 10H); IR ($CHCl_3$): 3550s, 1455m, 1430s; mass spectrum *m/e* (% relative intensity) 332 M^+ (100), 318 (17), 289 (8), 271 (8), 178 (4). Analysis: $C_{22}H_{20}O_3$ (C, H).

*2-n-Propyl-4-methoxy-5,6,7,8-tetrahydro-1-naphthol (**73c**)*

The workup involved stirring the methanol solution of the crude reaction mixture with a THF solution of $FeCl_3$-DMF complex (7 equiv.) for 1 h. The product was isolated by flash chromatography on silica gel with a 1/1/10 solvent mixture and obtained as a white solid in 72% yield ($R_f = 0.22$): m.p. 63–64°C; ^1H NMR: δ 0.99 (t, 3H, *J* 7.3 Hz), 1.64 (sextet, 2H, *J* 7.6 Hz), 1.73 (m, 2H), 1.78 (m, 2H), 2.54 (t, 2H, *J* 7.8 Hz), 2.58–2.63 (m, 4H), 3.75 (s, 3H), 4.19 (s, 1H), 6.46 (s, 1H); IR ($CDCl_3$) 3600s, 2925s, 1595s, 1260m, 1190s cm^{-1}; mass spectrum: *m/e* (% relative intensity) 220 M^+ (100), 191 (95); calcd. for $C_{14}H_{20}O_2$ *m/e* 220.1463, measured 220.1462. Two minor products also eluted from the silica gel column that were not characterized and were less than 5 weight % each.

Acknowledgement

This work was supported by the National Science Foundation under Grant CHE-8517103 and by the National Cancer Institute (PHS-CA 32974). The National Institute of Health has provided a predoctoral training grant for C.A.C. (No. GM 07183) and for K.L.F. (No. G.M. 07151). The NMR instruments used were funded in part by the NSF Chemical Instrumentation Program and by the NCI via the University of Chicago Cancer Research Center (CA-14599).

References

1 K.H. Dötz, Angew. Chem. Int. Ed. Engl., 14 (1975) 644.

2 (a) G.A. Peterson, F.A. Kunng, J.S. McCallum, and W.D. Wulff, Tetrahedron Lett., 28 (1987) 1381; (b) K.S. Chan and W.D. Wulff, J. Am. Chem. Soc., 108 (1986) 5229; (c) A. Yamashita, ibid., 107 (1985) 5823; (d) M.F. Semmelhack, J.J. Bozell, L. Keller, T. Sato, E.J. Spiess, W. Wulff, and A. Zask, Tetrahedron, 41 (1985) 5803; (e) K.H. Dötz and M. Popall, ibid., 41 (1985) 5797; (f) W.D. Wulff and D.C. Yang, J. Am. Chem. Soc., 106 (1984) 7565; (g) W.D. Wulff, K.S. Chan, and P.C. Tang, J. Org. Chem., 49 (1984) 2293; (h) W.D. Wulff and P.C. Tang, J. Am. Chem. Soc., 106 (1984) 434; (i) K.H. Dötz and W. Kuhn, Angew. Chem. Int. Ed. Engl., 22 (1983) 732; (j) K.H. Dötz, I. Pruskil, and J. Muhlemeier, Chem. Ber., 115 (1982) 1278.

3 For reviews of the chemistry of these complexes, see: (a) K.H. Dötz, H. Fischer, P. Hoffmann, F.R. Kreissl, U. Schubert and K. Weiss, Transition Metal Carbene Complexes, Verlag Chemie, Deerfield Beach, FL, 1984; (b) W.D. Wulff, P.C. Tang, K.S. Chan, J.S. McCallum, D.C. Yang, and S.R. Gibertson, Tetrahedron, 41 (1985) 5813; (c) K.H. Dötz, Angew. Chem. Int. Ed. Engl., 23 (1984) 587; (d) F.J. Brown, Prog. Inorg. Chem., 27 (1980) 1.

4 (a) A. Yamashita and A. Toy, Tetrahedron Lett., 27 (1986) 3471; (b) K.H. Dötz, J. Muhlemeier, U. Schubert and O. Orama, J. Organomet. Chem., 247 (1983) 187; (c) W.D. Wulff, P.C. Tang, J.S. McCallum, J. Am. Chem. Soc., 103 (1981) 7677.
5 K.H. Dötz, J. Organomet. Chem., 140 (1977) 177.
6 R.C. Combie, P.S. Rutledge, M. Tercel, and P.D. Woodgate, J. Organomet. Chem., 315 (1986) 171.
7 A. Yamashita, Tetrahedron Lett., 27 (1986) 5915.
8 For leading references to synthetic efforts directed towards the synthesis of olivin, see: R.W. Franck, V. Bhat, and C.S. Subramanian, J. Am. Chem. Soc., 108 (1986) 2455.
9 C. Reichardt, Solvent Effects in Organic Chemistry, Verlag Chemie, Deerfield Beach, FL, 1979, p. 17 and 271.
10 S. Tabinaga and E. Kotani, J. Am. Chem. Soc., 94 (1972) 309.
11 (a) K.H. Dötz and W. Strum, J. Organomet. Chem., 285 (1985) 205; (b) A. Yamashita and T.A. Scahill, Tetrahedron Lett., 23 (1982) 3765.
12 (a) K.H. Dötz and W. Sturm, J. Organomet. Chem., 310 (1986) C22; (b) K.H. Dötz and R. Dietz, ibid., 157 (1978) C55.
13 W.D. Wulff, S.R. Gilbertson, and J.P. Springer, J. Am. Chem. Soc., 108 (1986) 520.
14 J.D. Meinhart, B.D. Santarsiero, and R.H. Grubbs, J. Am. Chem. Soc., 108 (1981) 3318.
15 R.M. Silverstein, G.C. Baesler, and T.C. Morrill, Spectrometric identification of Organic Compounds, 4th edit., John Wiley, New York, NY, 1981, p. 123.
16 E. Muller and W. Winter, Justus Liebigs Ann. Chem., (1975) 605.
17 R.J. Carlier and F.A. Wagnier, Tetrahedron, (1975) 1841.
18 W.D. Wulff, R.W. Kaesler, G.A. Peterson, and P.C. Tang, J. Am. Chem. Soc., 107 (1985) 1060.
19 (a) H. Fischer, J. Muhlemeier, R. Markl, and K.H. Dötz, Chem. Ber., 115 (1982) 1355; (b) K.H. Dötz and B. Fugen-Koster, Chem. Ber., 113 (1980) 1449.
20 C.P. Casey in M. Jones, Jr., and R.A. Moss (Eds.), Reactive Intermediates, Vol. 2, Wiley, New York, 1981, p. 155.
21 (a) R.J. McKinny, T.H. Tulip, D.L. Thorn, T.S. Coolbough, and F.N. Tebbe, J. Am. Chem. Soc., 103 (1981) 5584; (b) T.R. Howard, J.B. Lee, and R.H. Grubbs, ibid., 102 (1980) 6876.
22 H.C. Foley, L.M. Strubinger, T.S. Targos, and G.L. Geoffrey, J. Am. Chem. Soc., 105 (1983) 3064.
23 (a) T. Mitsudo, H. Watanabe, K. Watanabe, Y. Watanabe, K. Kafuku and K. Nakatsu, Organometallics, 1 (1982) 612; (b) K. Nakatsu, T. Mitsudo, H. Nakanishi, Y. Watanabe and Y. Takegami, Chem. Lett., (1977) 1447.
24 P.C. Tang and W.D. Wulff, J. Am. Chem. Soc., 106 (1984) 1132.
25 N.A. Grabowski, R.P. Hughes, B.S. Jaynes and A.L. Rheingold, J. Chem. Soc., Chem. Commun., (1986) 1694.
26 (a) K.H. Dötz and J. Muhlemeier, Angew. Chem. Int. Ed. Engl., 21 (1982) 929; (b) K.H. Dötz and B. Fugen-Koster, Chem. Ber., 113 (1980) 1449.
27 W.D. Wulff and R.W. Kaesler, Organometallics, 4 (1985) 1461.
28 (a) J. Klimes and E. Weiss, Angew. Chem. Int. Ed. Engl., 21 (1982) 205; (b) A. Mayr, M.F. Asaro, T.J. Glines, J. Am. Chem. Soc., 109 (1987) 2215.
29 K.H. Dötz, W. Sturm, M. Popall, and J. Riede, J. Organomet. Chem., 277 (1984) 267.
30 (a) E.O. Fischer and H. Fischer, Chem. Ber., 107 (1974) 657; (b) C.F. Jewell, Jr., L.S. Liebeskind, and M. Williamson, J. Am. Chem. Soc., 107 (1985) 6715; (c) M.J. Wax and R.G. Bergman, ibid., 103 (1981) 7028; (d) S.L. Webb, C.M. Giandomennico and J. Halpern, ibid., 108 (1986) 345; (e) T.J. Katz and S.J. Lee, ibid., 102 (1980) 422; (f) W.D. Wulff, J.S. McCallum and F.A. Kunng, unpublished results; (g) D.J. Iverson, G. Hunter, J.F. Blount, J.R. Damewood, Jr., and K. Mislow, J. Am. Chem. Soc., 103 (1981) 6073; (h) K.H. Theopold, P.N. Becker and R.G. Bergman, ibid., 104 (1982) 5240; (i) E. Baciocchi, C. Rol, G.V. Sebastiani, and B. Serena, Tetrahedron Lett., 25 (1984) 1945.
31 E.O. Fischer, C.G. Kreiter, H.J. Kollmeier, J. Muller, and R.D. Fischer, J. Organomet. Chem., 28 (1971) 237.
32 See reference 1 for citations for the preparation of complex **9** which is now commercially available from Aldrich Chemical Company.
33 B. Halton, M. Kulig, M.A. Battiste, J. Perreten, D.M. Gibson, and G.W. Griffin, J. Am. Chem. Soc., 93 (1971) 2327.
34 R.L. Shriner and H.W. Johnston, Org. Syn., Coll. Vol. 3 (1962) 353.
35 R.H. Thomson, J. Chem. Soc., (1953) 1196.
36 B.M. Mikhailov, G.S. Ter-Sarkisyan, and N.A. Nikolaeva, Zh. Obschch. Khim., 41(8) (1971) 1721.

37 D.E. Kvalnes, J. Am. Chem. Soc., 56 (1934) 2478.
38 G. Wurm and U. Geres, Arch. Pharm., 317 (1984) 606.
39 G. Wurm, J. Baumann, U. Geres, and H. Schmidt, Arzneim. Forsch., 34 (1984) 652.
40 E.O. Fischer and J.A. Connor, J. Chem. Soc., (1969) 578.
41 C.F. Frisell and S.O. Lawesson, Org. Syn., Coll. Vol. 5 (1973) 924.
42 D.E. Shirley and J.P. Hendrix, J. Organomet. Chem., 28 (1971) 237.
43 For an alternate method for the preparation of complex **67**, see: W.D. Wulff, G.A. Peterson, W.E. Bauta, K.S. Chan, K.L. Faron, S.R. Gilbertson, R.W. Kaesler, D.C. Yang, and C.K. Murray, J. Org. Chem., 51 (1986) 277.
44 A.R. Chamberlin, J.E. Stenke, and F.T. Bond, J. Org. Chem., 43 (1978) 147.
45 G. Guillaumet, V. Lammel, G. Coudert, and P. Caubere, Tetrahedron, 30 (1974) 1289.
46 R.K. Boeckman and K.J. Bruca, Tetrahedron, 37 (1981) 3997.
47 J.A. Connors and E.M. Jones, J. Chem. Soc. A, (1971) 3368.