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Promotion of the Chromium Carbene Dötz Annulation Reaction Under Sonochemical and Dry State Adsorption Conditions

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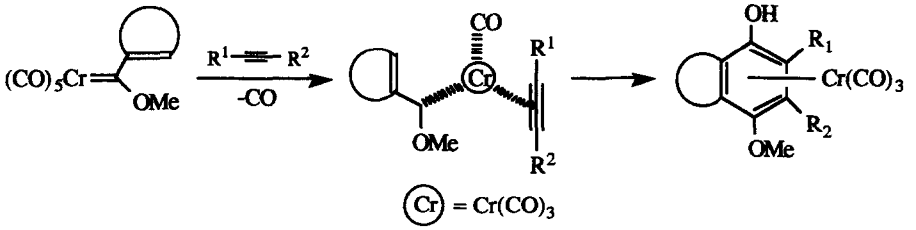
Abstract: The chromium carbene Dötz annulation reaction proceeds very rapidly in the presence of ultrasound giving good yields of quinone product on oxidative workup. Moreover, the yield of annulated product has been improved by adsorbing the reagents onto silica and heating at moderate temperatures. Both these modifications have proved to be successful for a variety of complexes and alkynes.

INTRODUCTION

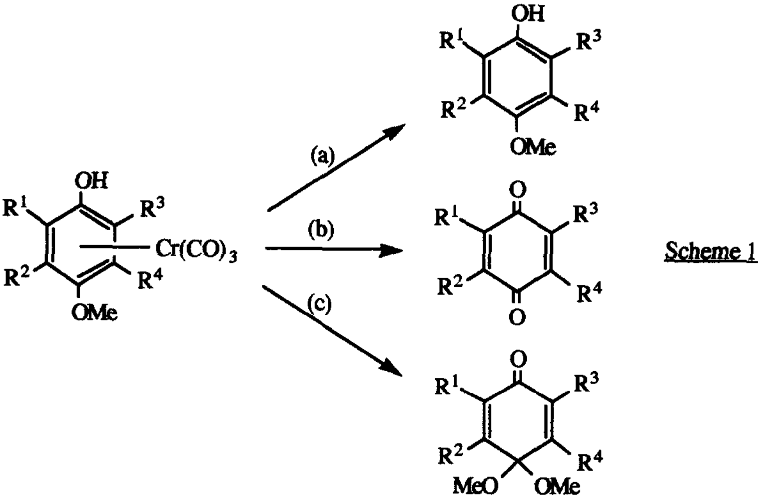
Transition metal carbene complexes have been the subject of intense study[1] since their discovery by Fischer in 1964.[2] In particular, the reaction of vinylchromium carbene complexes with alkynes (Dötz reaction), which allows the regioselective construction of highly substituted benzenoid compounds, has been extensively investigated and has found widespread use in organic synthesis.[3]

The mechanism of this reaction has been the subject of much debate[4,5] but it is clear that the first step involves the cleavage of a metal carbonyl bond followed by alkyne complexation.[6] This intermediate then undergoes a rapid cycloaddition reaction to give an aromatic six-membered ring which is π-bonded to the metal (Eq. 1). The metal complexed annulated product is air-sensitive and it is therefore common to employ an oxidative workup, as shown in Scheme 1, to isolate the de-metallated organic component[3c, 7] as either (a) the free naphthol (CO, Fe(III) or air), (b) the quinone (moist silica/air, Ce(IV)/H_2O, DDQ/H_2O, Ag_2O/H_2O or HNO_3/AcOH), or (c) the quinone monoketal (Ce(IV)/MeOH).



(Eq. 1)

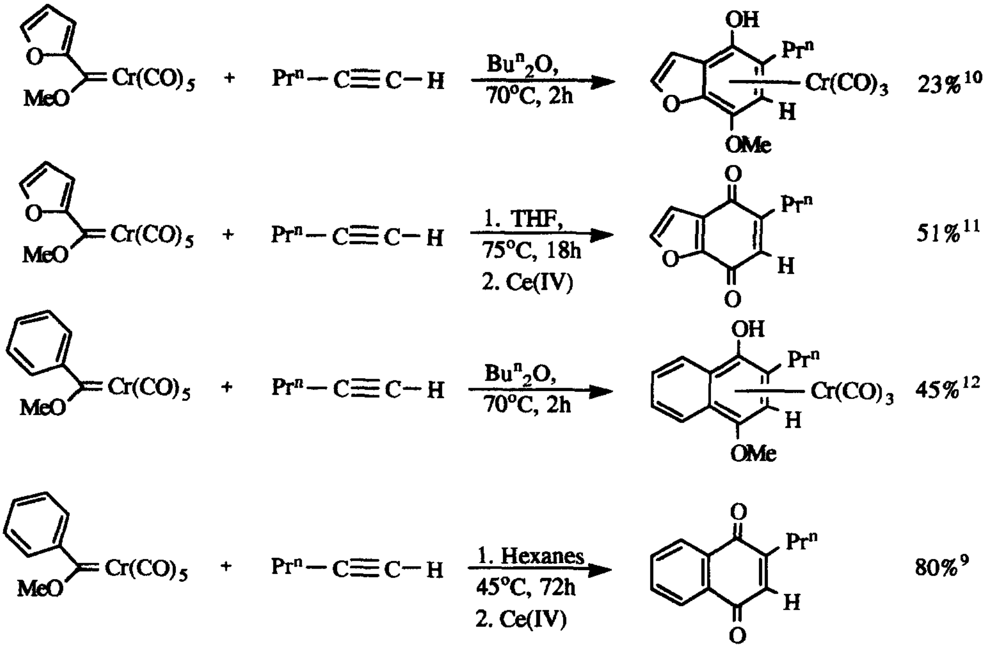
It has been shown that alkyne incorporation proceeds in a highly regioselective manner[8] where the bulkier



Scheme 1

substituent on the alkyne is placed, at least predominantly, adjacent to the phenolic hydroxyl group in the annulated product. More specifically, terminal alkynes give regioisomers in ratios of up to approximately 97:3.

The only substantial criticism of and major drawback to the Dötz annulation reaction is that, in some cases, the yield of cycloaddition product is only moderate. Recent attempts by Wulff[4, 9] to enhance the yields of cyclisation products, by careful manipulation of solvent, temperature and substrate concentration, have found some success but at the expense of longer reaction times. This is illustrated in Scheme 2 where a selection of comparative examples are laid out.



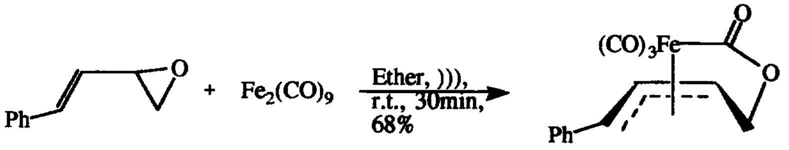
Scheme 2

RESULTS AND DISCUSSION

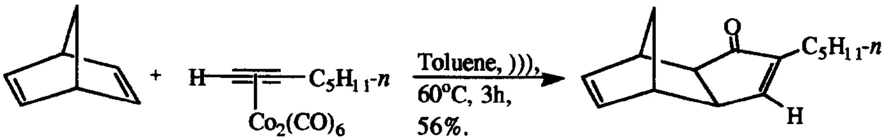
The first step of the annulation mechanism (*i.e.* loss of carbon monoxide followed by complexation) is known to be the rate determining step of the reaction.[6] We therefore envisaged that a fast metal-carbonyl cleavage would result in an accelerated cycloaddition reaction. Based on this assumption, a series of chromium carbene/alkyne annulation reactions were carried out under conditions which would facilitate this first step. Here we report upon two new methods which provide an overall general improvement for the Dötz cyclisation reaction in terms of both reaction rate and product yield.

Ultrasonication

The use of ultrasound techniques to break metal-carbon bonds quickly and efficiently is well documented.[13, 14] Furthermore this technique has recently found successful synthetic applications in the areas of iron lactone complex formation[15] and the Pauson-Khand cyclisation reaction, between alkynehexacarbonyldicobalt complexes and olefins.[16] In particular, the ultrasound mediated Pauson-Khand reaction was found to proceed very rapidly under mild conditions with, in some cases, a significant increase in product yield. Examples of both processes are shown below (Eq. 2&3).



(Eq. 2)[15b]

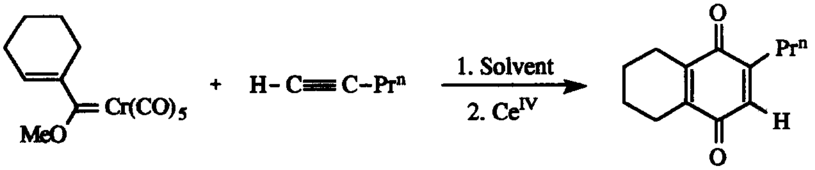


(Eq. 3)[16a]

Following the examination of a range of substrates we have now found that sonication readily promotes the Dötz cyclisation process at room temperature with completion of reaction in 5-25 minutes. Moreover, in all cases, yields of annulation products were comparable with those previously reported.[18]

Thus, the ultrasonication of a solution of metal carbene complex and alkyne in di-*n*-butyl ether resulted in a rapid cycloaddition reaction furnishing the six-membered ring product. In general, a mixture of both the metallated and de-metallated products was obtained but these were both readily converted into the appropriate air-stable naphthoquinone product by oxidation with ceric ammonium nitrate.

As outlined in Table 1, a series of chromium carbene complexes and alkynes were investigated in order to ascertain the generality of this technique. Initial studies proved that aromatic carbene complexes would undergo annulation very successfully (complexes **1a-c** and **2**) with alkynes. Furthermore, this technique also proved to be applicable to the less stable carbocyclic α,β-unsaturated carbene complexes. In the example laid out below (Eq. 4) the cyclohexenyl carbene complex **3** was sonicated in the presence of 1-pentyne until all of the starting complex had been consumed (as indicated by TLC). The reaction proceeded very efficiently inside 10 minutes to produce the expected tetrahydronaphthoquinone **6** in 75% yield on oxidative work-up. The same reaction when carried out thermally[9] (45°C) required 24 hours, to give the same product in a similar yield.



3 6

(Eq. 4)

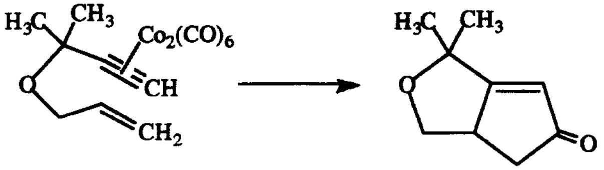
Ultrasonically: $Bu^n{}_2O$, 10 min., RT, 75%.
Thermally: CH_3CN, 24h, 45°C, 69%[9].

The source of ultrasound is crucial to the success of this reaction. It is known that a heterogeneous system can be affected by low intensity ultrasound, *e.g.* an ultrasonic bath, whereas a high intensity source is required for a homogeneous system.[13] Indeed, our homogeneous annulation reactions were attempted using an ultrasonic bath and were found to proceed extremely slowly. In all cases, the high intensity ultrasound required for enhanced reaction rates was supplied by a titanium horn (50W/20kHz).

This modification was found to be quite general and very successful for all complex/alkyne reactions attempted. Furthermore, the regiochemical control observed when using terminal alkynes did not differ from that found in the corresponding thermal reactions (see Table 1, entries 2 and 6).

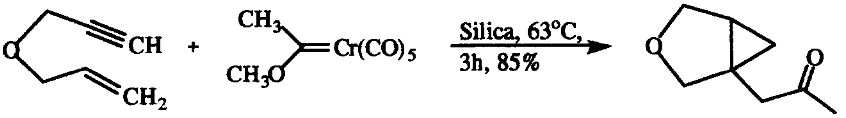
Dry State Adsorption

In addition to ultrasonication, solid state techniques have also been shown to promote metal mediated transformations where carbon monoxide cleavage is believed to be the initial step in the reaction mechanism. In particular, dry state adsorption techniques have been extensively applied to the Pauson-Khand reaction.[20] Cyclisations have been found to proceed very quickly under milder conditions, with shorter reaction times and considerable yield enhancements when both the alkynehexacarbonyldicobalt complexes and olefins are adsorbed onto silica or alumina. Furthermore, dry state adsorption (DSA) conditions have been used in the area of chromium carbene chemistry for the reaction of pentacarbonyl(methoxyethylidene)chromium with enynes to produce bicyclo[3.1.0]hexanes.[21] This intramolecular annulation was found to proceed only in the solid state, giving good to excellent yields of cyclised products. Examples of both cyclisation reactions are given in equations 5 and 6.



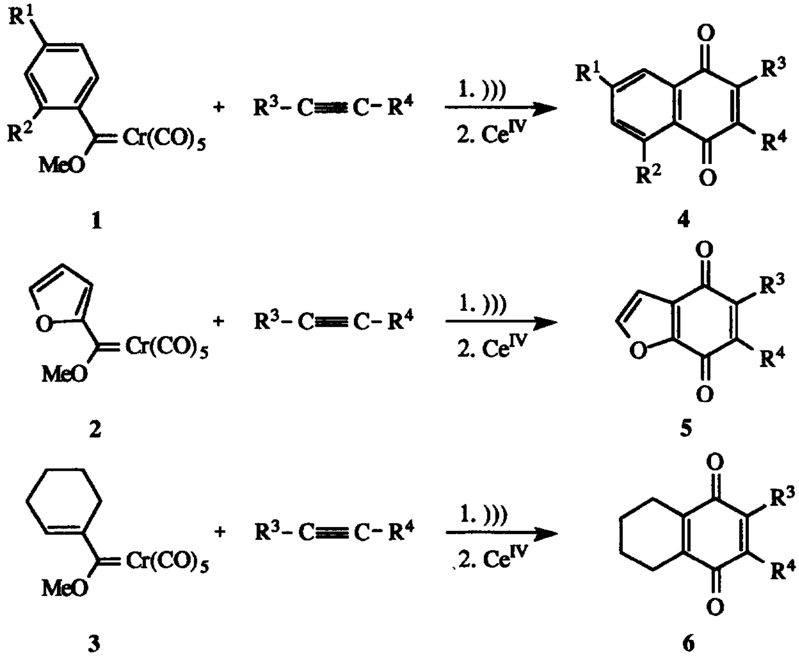
(Eq. 5)

Thermally: 60°C, CO, Isooctane, 24h, 29%[22]
Dry State Adsorption: 45°C, O_2, SiO_2, 30min, 76%[20c]



(Eq. 6)[21]

Table 1. Ultrasound Promoted Annulation Reactions.



Entry	Complex[a]	R^1	R^2	R^3	R^4	Product	Reaction time	Yield[b]
1	1a	Me	H	Ph	Ph	4a	20 min.	69%
2	1b	H	MeO	*n*-Pr	H	4b	5 min.	61%
3	1c	H	H	Ph	Ph	4c	20 min.	65%
4	1c	H	H	Ph	H	4d	10 min.	66%
5	1c	H	H	*n*-Pr	H	4e	15 min.	67%
6	2	--	--	*n*-Pr	H	5	25 min.	45%
7	3	--	--	*n*-Pr	H	6	10 min.	75%

[a] Chromium carbene complexes were obtained according to standard procedures reported in reference 17. [b] Isolated yields after chromatographic purification. See reference 18 for optimum literature yields and reaction conditions.

The results from our study, using a variety of chromium carbene complexes and alkynes, now demonstrate how dry state adsorption conditions serve to improve both the yield and rate of the Dötz annulation reaction. More specifically, the technique developed has resulted in promotion of the cyclisation process in times of 10min-3h. Furthermore, with the exception of one example, the reactions with silica proceeded in significantly higher yields than obtained using the more traditional "thermal" reaction conditions (see yields in parentheses in Table 2).

This solid state technique is practically convenient and, it is envisaged, could be applicable to synthesis on a larger scale. The carbene complex and alkyne were loaded onto the adsorbent and the resulting orange powder heated to temperatures of 40-80°C with stirring. Reaction progress was monitored by TLC analysis of extracts of small aliquots of the solid mixture. Following extraction and filtration the mixture was oxidised (ceric ammonium nitrate) at room temperature to yield the quinone products after standard purification.

The generality of this method was examined with three solid supports (SiO_2, $MgSO_4$, and Al_2O_3). As illustrated in Table 2, all annulation reactions proceeded most efficiently when carried out on silica giving products in high yields under mild conditions. In only one case was the reaction yield lower than that of the known "thermal" reaction (Table 2, Entry 4). The volatility of the alkyne (1-pentyne) used in this reaction may be responsible for this comparatively low yield. It is anticipated that this may be improved by performing the reaction at a lower temperature.

Again, as can be noted from Table 2, magnesium sulphate also allowed the reaction to proceed in good yields in two of the three cases tried. However, alumina did not give a favourable product yield in the one reported example, despite the relatively fast reaction rate.

It has been postulated that interaction with donor centres on the surface of such adsorbents facilitate metal-carbonyl cleavage.[20h] Furthermore, as previously discussed, the dissociation of a carbon monoxide ligand from the chromium centre is thought to be the rate determining step during Dötz cyclisation reactions. It is therefore likely that the DSA technique employed mildly promotes this primary ligand exchange process and, in so doing, the mechanistic sequence leading to the annulated products.

CONCLUSIONS

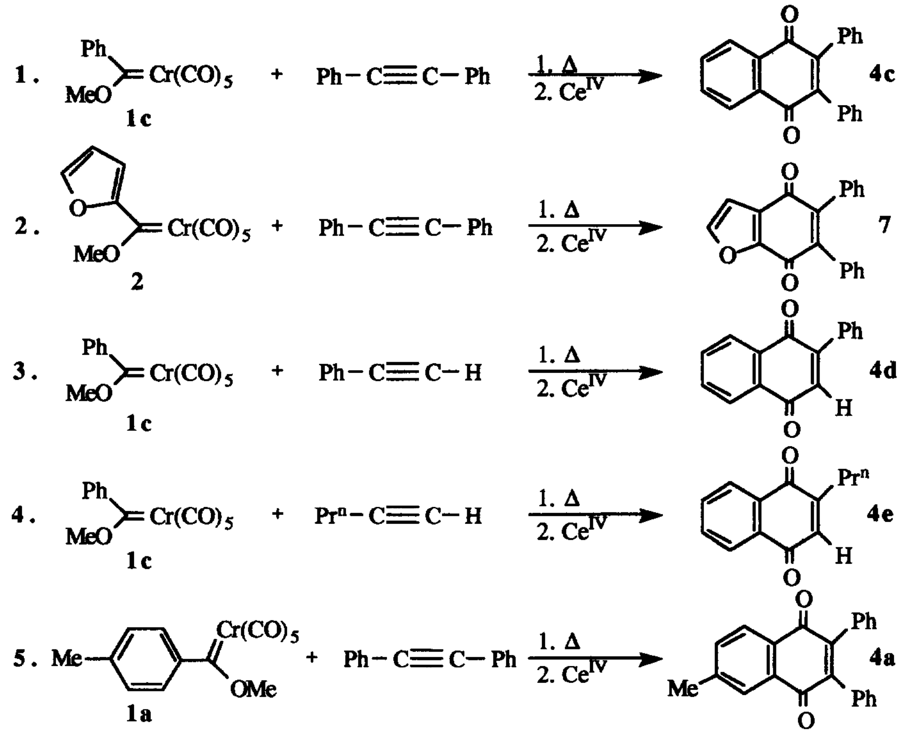
In general, the chromium carbene Dötz annulation reaction can be carried out very efficiently under the developed conditions of both ultrasound and DSA.

Reactions mediated by titanium horn ultrasonication proceed with greatly enhanced rates (under 25min) to give product yields which are comparable to those observed under "thermal" conditions. This technique is equally successful when applied to aryl, heteroaryl, and α,β-unsaturated carbocyclic complexes. Further studies, using this technique with aminocarbene complexes are underway.

The Dötz cyclisation reaction is also promoted in the solid state. In particular, when silica is employed as the adsorbent the DSA techniques developed serve to facilitate reaction to give annulated products in yields which are generally higher than previously obtained. A further advantage to this technique is that, in all cases tried, reactions were complete within 3h. Further applications of this technique to alkenylmethoxycarbene complexes, both aryl- and alkenylaminocarbene complexes, and more volatile alkynes are currently under investigation.

Overall, both techniques described here provide novel, practical and versatile methods for performing the Dötz annulation reaction.

Table 2. DSA Promoted Annulation Reactions.



Entry[a]	Adsorbent	Temp.(°C)	Time	Yield[b]
1	SiO_2	40-50	180min	86% (62%, ref. 23)
	$MgSO_4$	50	90min	77%
	Al_2O_3	60-65	10min	15%
2	SiO_2	50-60	120min	74% (19%, ref. 24)
	$MgSO_4$	70-80	180min	43%
3	SiO_2	60-65	90min.	81% (67%, ref. 9)
	$MgSO_4$	60-70	90min	18%
4	SiO_2	60	10min	51% (80%, ref. 9)
5	SiO_2	50	180min	70% (40%, ref. 24)

[a] Chromium carbene complexes were obtained according to standard procedures reported in reference 17. [b] Isolated yields on chromatographic purification. Literature yields in parentheses. See reference 25 for literature reaction conditions and times.

EXPERIMENTAL

General information

All reagents were obtained from commercial suppliers and used without further purification unless otherwise indicated. Petrol refers to petroleum ether, bp 40-60°C. Cerium (IV) oxidations employed a 0.5M solution of ceric ammonium nitrate in 0.1M aqueous nitric acid. Solid state reactions were performed on silica (230-400 mesh), anhydrous magnesium sulphate or alumina, which was neutralised with ethyl acetate prior to use. Di-*n*-butyl ether was distilled from $LiAlH_4$, phenylacetylene and 1-pentyne were also distilled prior to use. Chromatographic purification was carried out on silica gel (230-400 mesh) by flash techniques. Proton and ^{13}C nmr were obtained on a 250MHz Bruker WM 250 spectrometer or a 400MHz Bruker WM 400 instrument. In ^{13}C nmr jmod spectra, "up" indicates C and CH_2; "down" indicates CH and CH_3. Infrared spectra were run on a Perkin-Elmer 397 spectrometer, Fourier transform infrared data were obtained on a Mattson 1000 instrument. High resolution mass spectra were recorded on an AEI MS 9 double focussing spectrometer using an Elliot 905 computer based system; relative peak intensities are indicated in parenthesis. Elemental analysis (for new compounds) was carried out on a Carlo Erba 1106 CHN analyser. Sonications were carried out using a Vibracell^{TM} VC 50 titanium horn operating at 50W/20kHz output. Melting points were determined on an electrothermal melting point apparatus and are uncorrected.

General procedure for ultrasound mediated annulation reactions.

The titanium horn was immersed in a solution of the carbene complex and alkyne (1-1.5 equiv.) in 4ml of di-*n*-butyl ether. The solution was subjected to ultrasound until all of the starting complex had been consumed (as indicated by TLC). The probe was washed with ether and the washings combined with the reaction mixture. On removal of the solvent *in vacuo*, the residue was taken up in 10ml of ether and treated with 8 equivalents of Ce^{IV} solution. Oxidations were complete by stirring at room temperature for 30min. The ether layer was separated and the aqueous layer extracted with more ether (3x10ml). The combined organic extracts were washed with brine, dried over magnesium sulphate and purified chromatographically.

2,3-Diphenyl-6-methyl-1,4-naphthoquinone 4a.

Following the general procedure complex **1a** (51mg, 0.156mmol) and diphenylacetylene (34mg, 0.191mmol) were subjected to sonication for 20min. Eluent for silica chromatography: *n*-hexane/dichloromethane (2:1). Compound **4a** was obtained as a yellow crystalline solid (35mg, 69%), mp 135-136°C. FTIR (CH_2Cl_2): 1665, 1610cm^{-1}; ^1H nmr ($CDCl_3$): δ 2.55 (3H, s), 7.08-8.07ppm (13H, m); ^{13}C nmr ($CDCl_3$): δ 22.13 (down), 127.04 (down), 127.09 (down), 127.78 (down), 127.80 (down), 128.34 (down), 130.16 (up), 130.74 (down), 132.28 (up), 133.56 (up), 133.58 (up), 134.81 (down), 145.18 (up), 145.83 (up), 145.92 (up), 184.83 (up), 185.27ppm (up); m/e (M^+) 324.12 (100). Anal. Calc. for $C_{23}H_{16}O_2$: C 85.15, H 4.98%; found: C 85.31, H 4.89%.

2-*n*-Propyl-5-methoxy-1,4-naphthoquinone 4b.[9]

Following the general procedure complex **1b** (56mg, 0.164mmol) and 1-pentyne (17mg, 0.250mmol) were subjected to sonication for 5 min. Eluent for silica chromatography: dichloromethane/ether/*n*-hexane (1:1:2). Compound **4b** was obtained as a yellow crystalline solid (23mg, 61%), mp 64-65°C (Lit. mp[26] 64°C). FTIR (CH_2Cl_2): 1668cm^{-1}; ^1H nmr ($CDCl_3$): δ 0.99 (3H, t, J=7.4Hz), 1.60 (2H, sextet, J=7.4Hz), 2.49 (2H, t, J=8.0Hz), 4.00 (3H, s), 6.68 (1H, s), 7.28 (1H, d, J=8.4Hz), 7.65 (1H, t, J=8.0Hz), 7.75ppm (1H, d, J=7.6Hz).

2,3-Diphenyl-1,4-naphthoquinone 4c.[9]

Following the general procedure complex **1c** (106mg, 0.440mmol) and diphenylacetylene (102mg, 0.572mmol) were subjected to sonication for 20 min. Eluent for silica chromatography: petrol/dichloromethane (3:2). Compound **4c** was obtained as a yellow crystalline solid (89mg, 65%), mp 139-140°C (Lit. mp[27] 141-142°C). FTIR (CH_2Cl_2): 1670, 1601cm^{-1}; ^1H nmr ($CDCl_3$): δ 7.10 (4H, m), 7.23 (6H, m), 7.81 (2H, m), 8.21ppm (2H, m).

2-Phenyl-1,4-naphthoquinone 4d.[9]

Following the general procedure complex **1c** (197mg, 0.631mmol) and phenylacetylene (93mg, 0.910mmol) were subjected to sonication for 10 min. Eluent for silica chromatography: petrol/dichloromethane (3:2). Compound **4d** was obtained as a yellow crystalline solid (97mg, 66%), mp 109-110°C (Lit. mp[28] 111-112°C). IR (KBr): 1660, 1590cm^{-1}; ^1H nmr ($CDCl_3$): δ 7.09 (1H, s), 7.49 (3H, m), 7.58 (2H, m), 7.79 (2H, m), 8.11-8.22ppm (2H, m).

2-*n*-Propyl-1,4-naphthoquinone 4e.[9]

Following the general procedure complex **1c** (219mg, 0.701mmol) and 1-pentyne (69mg, 1.013mmol) were subjected to sonication for 15 min. Eluent for silica chromatography: petrol/dichloromethane (2:1). Compound **4e** was obtained as a yellow crystalline solid (94mg, 67%), mp 38-39°C (Lit. mp[29] 37-39°C). FTIR (CH_2Cl_2): 1685cm^{-1}; ^1H nmr ($CDCl_3$): δ 1.00 (3H, t, J=7.4Hz), 1.62 (2H, sextet, J=7.4Hz), 2.53 (2H, t, J=7.3Hz), 6.48 (1H, s), 7.72 (2H, m), 8.01-8.11ppm (2H, m).

5-*n*-Propyl-benzofuran-4,7-dione 5.[11]

Following the general procedure complex **2** (118mg, 0.390mmol) and 1-pentyne (35mg, 0.514mmol) were subjected to sonication for 25 min. Eluent for silica chromatography: ethyl acetate/*n*-hexane (1:5). Compound **5** was obtained as a yellow crystalline solid (33mg, 45%). IR ($CHCl_3$): 1670cm^{-1}; ^1H nmr ($CDCl_3$): δ 0.99 (3H, t, J=7.4Hz), 1.58 (2H, sextet, J=7.7Hz), 2.47 (2H, dt, J=7.6, 1.4Hz), 6.49 (1H, t, J=1.4Hz), 6.85 (1H, d, J=1.8Hz), 7.67ppm (1H, d, J=1.9Hz).

2-*n*-Propyl-5,6,7,8-tetrahydro-1,4-napthoquinone 6.[9]

Following the general procedure complex **3** (99mg, 0.313mmol) and 1-pentyne (35mg, 0.514mmol) were subjected to sonication for 10 min. Eluent for silica chromatography: petrol/dichloromethane (2:1). Compound **6** was obtained as a yellow crystalline solid (48mg, 75%). FTIR (CH_2Cl_2): 1659cm^{-1}; ^1H nmr ($CDCl_3$): δ 0.96 (3H, t, J=7.4Hz), 1.53 (2H, q, J=7.5Hz), 1.69 (4H, m), 2.34-2.44 (6H, m), 6.48ppm (1H, s).

General procedure for annulation under DSA conditions.

A suspension of carbene complex, adsorbent (10g/mmol of alkyne) and alkyne in hexane or ether was stirred for 5 min at room temperature and the solvent removed *in vacuo*. In the case of volatile alkynes (*ie* 1-pentyne) the alkyne was simply added after the complex had been adsorbed onto the solid support. The round-bottom flask containing the resulting orange powder was purged with nitrogen and immersed in a heated oil bath and stirred until all of the complex had been consumed (as indicated by TLC analysis of extracts of small aliquots of solid mixture). On completion of reaction, the adsorbent was extracted with ether and filtered through a pad of Kieselguhr. The resulting crude phenol product was oxidatively worked up and purified in the same manner as described for ultrasound mediated annulations.

Physical and spectrochemical data are not cited for those compounds previously described.

2,3-Diphenyl-1,4-naphthoquinone 4c.

Silica mediated annulation: Following the general procedure complex **1c** (65mg, 0.208mmol), diphenylacetylene (46mg, 0.258mmol) and silica (2.58g) were stirred at 40-50°C for 3h. Silica chromatography yielded compound **4c** (56mg, 86%).

Magnesium sulphate mediated annulation: Following the general procedure complex **1c** (21mg, 0.067mmol), diphenylacetylene (12mg, 0.067mmol) and magnesium sulphate (0.67g) were stirred at 50°C for 90min. Silica chromatography yielded compound **4c** (16mg, 77%).

Alumina mediated annulation: Following the general procedure complex **1c** (61mg, 0.195mmol), diphenylacetylene (42mg, 0.236mmol) and alumina (2.36g) were stirred at 60-65°C for 10min. Silica chromatography yielded compound **4c** (9mg, 15%).

5,6-Diphenyl-benzofuran-4,7-dione 7.

Silica mediated annulation: Following the general procedure complex 2 (75mg, 0.248mmol), diphenylacetylene (57mg, 0.320mmol) and silica (3.20g) were stirred at 50-60°C for 2h. Eluent for silica chromatography: dichloromethane/petrol (7:3). Compound 7 was obtained as an orange crystalline solid (55mg, 74%), mp 179-180°C. FTIR (CH_2Cl_2): 1677 cm^{-1}; ^{1}H nmr ($CDCl_3$): δ 6.95-7.04 (5H, m), 7.18-7.27 (6H, m), 7.77ppm (1H, d, J=1.8Hz); ^{13}C nmr ($CDCl_3$): δ 108.51, 127.83, 127.87, 128.28, 128.48, 128.54, 130.90, 132.45, 132.97, 143.48, 148.42, 151.06, 175.44, 182.47ppm; m/e (M^+) 300.08 (100). Anal. Calc. for $C_{20}H_{12}O_3$: C 79.98, H 4.04%; found: C 79.76, H 3.93%.

Magnesium sulphate mediated annulation: Following the general procedure complex 2 (60mg, 0.199mmol), diphenylacetylene (49mg, 0.275mmol) and magnesium sulphate (2.75g) were stirred at 70-80°C for 3h. Silica chromatography yielded compound 7 (26mg, 43%).

2-Phenyl-1,4-naphthoquinone 4d.

Silica mediated annulation: Following the general procedure complex **1c** (142mg, 0.455mmol), phenylacetylene (93mg, 0.910mmol) and silica (9.10g) were stirred at 60-65°C for 90min. Silica chromatography yielded compound **4d** (87mg, 81%).

Magnesium sulphate mediated annulation: Following the general procedure complex **1c** (72mg, 0.231mmol), phenylacetylene (46mg, 0.450mmol) and magnesium sulphate (4.55g) were stirred at 60-70°C for 90min. Silica chromatography yielded compound **4d** (10mg, 18%).

2-*n*-Propyl-1,4-naphthoquinone 4e.

Silica mediated annulation: Following the general procedure complex **1c** (166mg, 0.532mmol), 1-pentyne (69mg, 1.013mmol) and silica (10.13g) were stirred at 60°C for 10min. Silica chromatography yielded compound **4e** (54mg, 51%).

2,3-Diphenyl-6-methyl-1,4-naphthoquinone 4a.

Silica mediated annulation: Following the general procedure complex **1a** (56mg, 0.172mmol), diphenylacetylene (43mg, 0.241mmol) and silica (2.41g) were stirred at 50°C for 3h. Silica chromatography yielded compound **4a** (39mg, 70%).

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18. Literature conditions and yields for the reactions listed in **Table 1** are as follows: **Entry 1**; 45°C, *n*-Bu$_2$O, 2h, 40% of the parent tricarbonyl chromium phenol complex, ref. 10. **Entry 2**; 45°C, THF, 16-24h, 64%, ref. 4. **Entry 3**; 45°C, *n*-Bu$_2$O, 3h, 62% of the parent tricarbonyl chromium phenol complex, ref. 19. **Entry 4**; 45°C, THF, 23h, 67%, ref. 9. **Entry 5**; 45°C, hexanes, 72h, 80%, ref. 9. **Entry 6**; 75°C, THF, 18h, 51%, ref. 11. **Entry 7**; 45°C, CH$_3$CN, 24h, 69%, ref. 9.
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23. This yield refers to the parent tricarbonylchromium phenol complex. See ref. 19.
24. This yield refers to the parent tricarbonylchromium phenol complex. See ref. 10.
25. Literature conditions and times for the reactions listed in **Table 2** are as follows: **Entry 1**; 45°C, *n*-Bu_2O, 3h, ref. 19. **Entry 2**; 80°C, *n*-Bu_2O, 2.5h, ref. 10. **Entry 3**; 45°C, THF, 23h, ref. 9. **Entry 4**; 45°C, hexanes, 72h, ref. 9. **Entry 5**; 45°C, *n*-Bu_2O, 2h, ref. 10.
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