Conversion of Adducts formed from Tricarbonyl(vinylketene)iron(0) Complexes and Alkynes into Cyclopentenediones and Phenols

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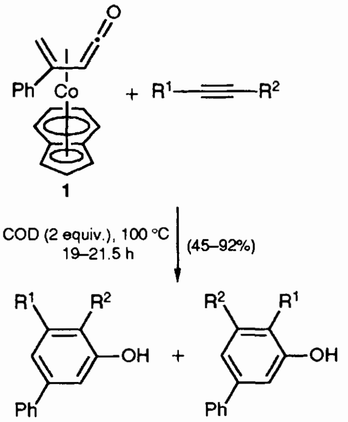
Thermolysis of adducts formed from tricarbonyl(vinylketene)iron(0) complexes and alkynes leads to either cyclopentenediones or phenols and its outcome is controlled by the electronic properties of the C-1 substituent of the adduct; the phenols may be synthesised directly and regioselectively from tricarbonyl(vinylketene)iron(0) complexes and electron-rich alkynes.

In view of the pivotal role postulated for chromium-centred vinylketene complexes in the mechanistically-fascinating and synthetically-attractive reactions which occur between chromium Fischer carbene complexes and alkynes,[1] there has been considerable interest in recent years in the reactivity of transition metal complexes of vinylketenes. In particular, their reactivity towards alkynes has been the subject of significant attention. Thus, it has been demonstrated that the cobalt-centred vinylketene complex **1** reacts with hex-1-yne, pent-1-yne, dimethyl acetylenedicarboxylate and ethyl but-2-ynoate to give phenols.[2,3] In contrast the chromium-centred complex **2** has been shown to react with diethylpropynylamine to give a [2 + 2] cycloadduct **3**, whilst the closely-related chromium centred complex **4** has been shown to react with pent-1-yne to give the cyclopentenedione **5** and the isomeric indanols **6** and **7** after a reductive work-up.[4]



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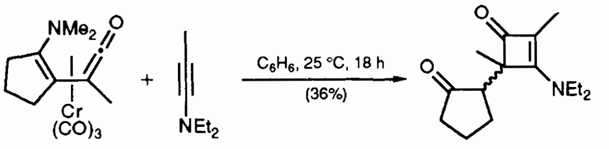
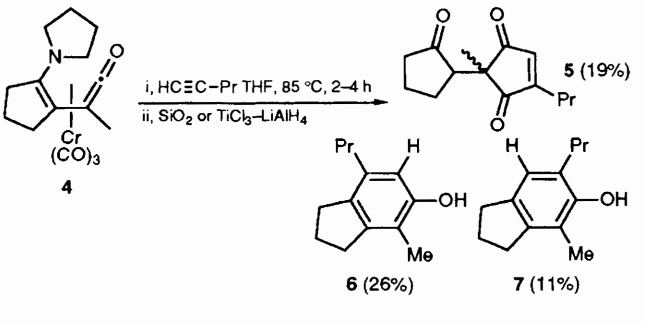


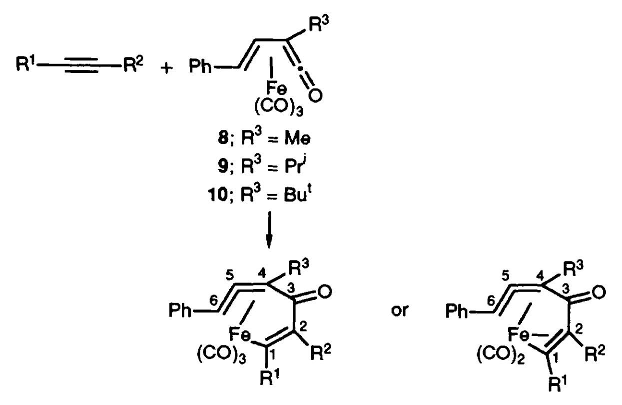
2 **3**



4 **6** (26%) **7** (11%)

Intrigued by the range of products obtained from the reactions between cobalt- and chromium-centred vinylketene complexes and alkynes, we initiated an investigation of the reactivity of readily-accessible iron-centred vinylketene complexes **8–10**[5] towards alkynes. Initial experiments revealed that addition of alkynes to these iron-centred vinylketene complexes led to efficient and regiospecific formation of stable and isolable adducts exemplified by **11–14**.[6] In principle, these adducts are potential precursors of all of the products observed in the cobalt and chromium systems outlined above. Reductive elimination across C-1 and C-4 would generate cyclobutenones, migration of C-1 to a carbonyl ligand followed by reductive elimination at C-4 or migration of C-4 to a carbonyl ligand followed by reductive elimination at C-1 would generate cyclopentenediones, and reductive elimination across C-1 and C-6 followed by aromatisation would give phenols. Thus, it was of significant interest to thermolyse adducts **11–14** and identify any organic products generated. The results of these experiments, which reveal that these adducts are precursors of cyclopentenediones and phenols and that the outcome of the thermolysis is controlled by the nature of the C-1 substituent on the adduct, are reported below.

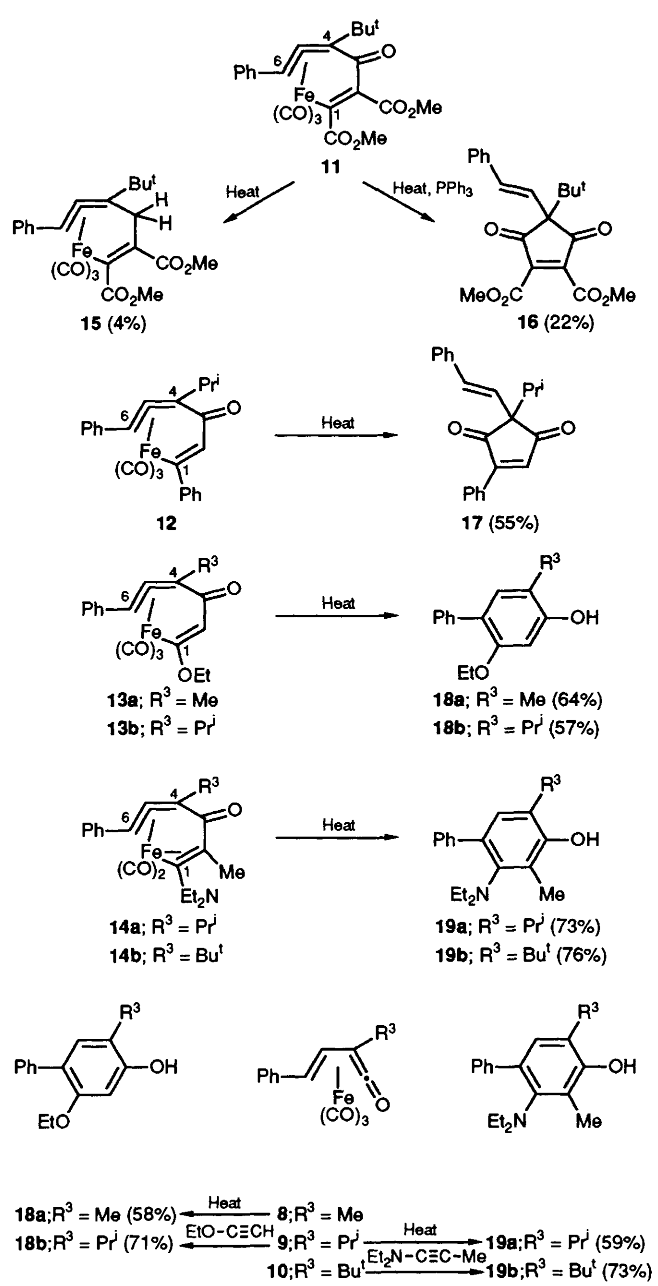
Initial investigations focused on adduct **11** which is readily derived from the vinylketene complex **10** and dimethyl acetylenedicarboxylate by stirring them together at 80 °C for 1.75 h.[6] Thermolysis of **11** at 95 °C for 17.5 h in toluene led to an almost intractable mixture of organic and inorganic materials from which it eventually proved possible to isolate



8; R^3 = Me
9; R^3 = Pr^i
10; R^3 = Bu^t

	R^1	R^2	R^3
11	CO_2Me	CO_2Me	Bu^t
12	Ph	H	Pr^i
13a	OEt	H	Me
13b	OEt	H	Pr^i

	R^1	R^2	R^3
14a	Et_2N	Me	Pr^i
14b	Et_2N	Me	Bu^t



the reduced complex **15** in very low yield. To the best of our knowledge the product mixture did not contain any simple organic compounds derived directly from adduct **11**. After several different reaction temperatures and times had given similar results, the effect of adding 2.2 equiv. of PPh_3 to the reaction mixture was examined. In this case, thermolysis at 70–80 °C for 7 days in toluene gave an organic product which was isolated and identified as the cyclopentenedione **16**.† [Note that cyclopentenedione **16** has been constructed from the same components as the cyclopentenedione **5** (*i.e.* a vinylketene complex, an alkyne and a molecule of carbon monoxide) albeit using more forcing conditions in the second step.]

Attention then turned to adduct **12** which was formed by treating vinylketene complex **9** with phenylacetylene.[6] In contrast to the problems encountered with complex **11**, thermolysis alone (85 °C, 3 days, toluene) led to five-membered ring formation and the isolation of cyclopentenedione **17** in relatively good yield.

Complexes **13a** and **b**, which were synthesised by treating vinylketene complexes **8** and **9** with the oxygen-substituted alkyne ethyl ethynyl ether,[6] were examined next. Thermolysis of **13a** and **b** (95 °C, 6 days, toluene) and work-up led to the isolation of organic compounds, which were identified as the phenols **18a** and **b**.† Similarly, when the dicarbonyliron(0) adducts **14a** and **b**, which were formed from the vinylketene complexes **9** and **10** and diethylpropynylamine,[6] were thermolysed (95 °C, 6 and 11 days respectively, toluene), phenols **19a** and **b** were produced and isolated in good yield. Careful examination of the crude product mixtures from which the four phenols were isolated established that the corresponding cyclopentenediones had not been formed in any of these reactions.

The results described above reveal that the outcome of thermolysis of the adducts is governed by the substituent on C-1 of the adduct. Thus, adducts bearing C-1 substituents capable of significant electron donation give phenols whilst adducts bearing C-1 substituents incapable of significant electron donation give cyclopentenediones. It is proposed that the strongly electron-donating substituents reduce the strength of the iron-C-1 bond (by competing effectively with a filled metal orbital for interaction with the C=C–C=O fragment) and thus facilitate reductive elimination across C-1 and C-6. The stronger iron–C-1 bonds of adducts **4** and **5** render this pathway less favourable and migration of C-4 to a carbonyl ligand becomes accessible. Reductive elimination between the acyl ligand so formed and C-1 of complex **12** relatively readily produces cyclopentenedione **17** whilst reductive elimination of the acyl ligand formed from complex **11** and C-1 is inaccessible under simple thermolysis conditions because of the strength of the iron–C-1 bond in this system.

Finally, it was demonstrated that tricarbonyliron(0) complexes can be converted directly into regiochemically pure phenols simply by heating with an appropriate alkyne. Thus, vinylketene complexes **8** and **9** gave phenols **18a** and **b** when they were heated with ethoxy ethynyl ether (80 °C, 5 and 14 days respectively, toluene) and vinylketene complexes **9** and **10** gave phenols **19a** and **b** when they were treated with diethylpropynylamine (85 and 80 °C respectively, 7 and 15 days respectively, toluene).

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† Novel compounds **15–19** all gave IR, ^1H NMR, ^{13}C NMR and low resolution mass spectroscopic data consistent with their proposed structures. Satisfactory microanalytical data and/or high resolution MS data were also obtained for these compounds.

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