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The cycloaddition reactions of 2-ethoxy-3-phenylvinylketene iron(0) with alkynes to yield catechol derivatives

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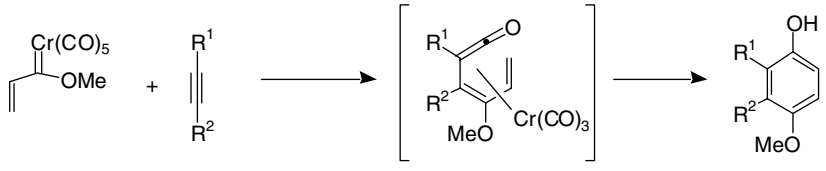
Abstract—Tricarbonyl(3-ethoxy-4-phenyl-1-oxa-1,2,4-pentatrienone) iron(0) reacts with a variety of electron deficient and electron rich alkynes to produce catechol monoethyl ethers in moderate to good yield. Steric hindrance of the alkyne often exerts a stronger influence than electronic factors in determining the product distribution. The reaction with several alkyl, silyl, and aryl alkynes produced alkyne trimers as the major products.

Vinylketenes (1-oxa-1,2,4-pentatrienes or 1,4-butadien-1-ones) are extremely reactive, rarely isolated compounds that have emerged as an important class of reagents in organic synthesis.[1] Their transition metal derivatives, which are sometimes isolable, constitute an important class of organometallic compounds that have been demonstrated to undergo a number of mechanistically and synthetically interesting transformations.[2] Particularly appealing is the notion that highly substituted phenols may be accessed by reaction of these complexes with alkynes. This represents an important complement to the Dötz benzannulation reaction that produces hydroquinone derivatives from chromium carbene complexes upon reaction with alkynes.[3] (Scheme 1) The proposed mechanism for this valuable synthetic reaction involves the intermediacy of a vinylketene chromium complex that undergoes an electrocyclic ring closure to give the *p*-alkoxyphenol. Merlic developed an important variation using photochemically generated dienylketene complexes that produce *o*-alkoxyphenols and catechol structures.[4] Wulff reported a phenol synthesis upon reaction of pentyne with an isolated chromium(0) vinylketene complex.[5] The electron rich alkyne, *N*,*N*-diethylaminopropyne produced the cyclobutene derived from a [2+2] cycloaddition reaction with the vinylketene.[5] Liebeskind reported the first general synthesis of phenols from the reaction of alkynes with isolated cobalt(I) vinylketene complexes, which were prepared from cyclobutenones, having made the observation that a methyl group in position 5 severely compromised the generality of the reaction.[6] Gibson (née Thomas) reported the addition reactions of 3-alkyl-5-phenyl-1-oxa-1,2,4-pentatriene iron(0) complexes with alkynes, which produced η^3-allyl-η^1-vinylacyl iron derivatives



Scheme 1. Benzannulation reaction of chromium carbene complexes and alkynes.

Keywords: Vinylketene complex; Iron; Cycloaddition; Alkynes; Phenols.
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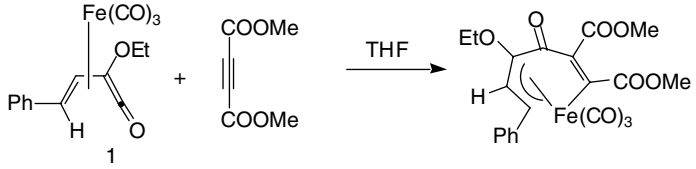
through insertion of the alkyne into the acyl iron bond. These isolable complexes were then converted to phenols, furan derivatives, or cyclopentenediones. With electron rich alkynes phenols were obtained directly without isolation of the intermediate complex.[7]

We report herein our preliminary findings during the exploration of the significant potential of 2-alkoxyvinylketenes as formal equivalents to dienes upon reaction with alkynes to form substituted catechol[8] or *o*-quinone derivatives. Although vinylketene complexes bearing an oxygen substituent at C-2 can be accessed through several complementary approaches, reports of their reactions with alkynes are non-existent. In our studies, the complexes were synthesized via vinyllithium reagents that were prepared from vinyl bromides by established methods.[9] Reaction of the lithium reagents with iron pentacarbonyl produced the tetracarbonyl iron acylates analogous to those prepared from vinyllithium compounds derived from vinyltin reagents,[10] or via reaction of tetracarbonyl ferrates with α,β-unsaturated acyl halides.[11] Addition of triethyloxonium tetrafluoroborate (Meerwein's salt) in the presence of HMPA provided the vinylketene complexes in moderate yield.[12–14]

In the reactions of vinylketene iron complexes with alkynes that were reported by Gibson, steric effects played an important role that was sometimes balanced by electronic influences. Consistent with this was our observation that the reaction of 3-ethoxy-5-phenyl-1-oxa-1,2,4-pentatrienone, **1**, and dimethyl acetylene dicarboxylate produced the η^3-allyl-η^1-acyl iron complex in 27% yield after 0.5 h in refluxing THF (Scheme 2).[12] Continued heating resulted in non-specific decomposition. We believed that readily available 3-ethoxy-4-phenyl-1-oxa-1,2,4-pentatriene, **2**,[15] would suffer no steric encumbrance, at position 5, to reductive elimination of the allyl acyl complex to provide the phenol and was gratified to find that mild conditions were sufficient to obtain moderate yields of phenols from reactions with alkynes. The results of our efforts at exploring the scope of the benzannulation process are summarized in Table 1.[16]

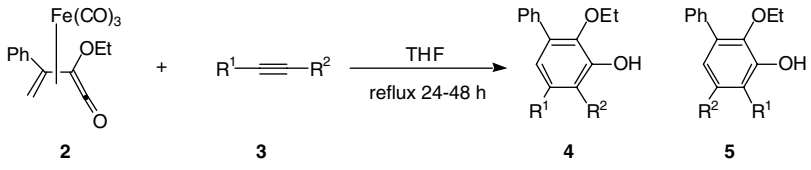
In our hands, regioselectivities were often good, but were sensitive to minor structural differences. The results of successful benzannulations are summarized in Table 1. The reaction proceeds readily in refluxing tetrahydrofuran (THF) over 24–48 h. Toluene proved to be a poor solvent for this system, leading to reduced yields and complicated mixtures. The major by-products were the alkyne trimers, both symmetrical and unsymmetrical, which were detected as impurities in NMR spectra and GC–MS of crude samples. Analysis of crude NMR spectra also indicated the formation of intermediates such as those described by Gibson, which are readily detected by the diasteropicity of CH_2 protons (ABX_3 patterns around 4 and 1.2 ppm). In our studies, we were unable to isolate the η^3-allyl-η^1-vinylacyl iron complexes in analytically pure form. Esters, a ketone, and an acetylenic ether all provided catechol monoethyl ethers.

The electron rich alkyne, ethyl ethynyl ether provided the phenol with the ethoxy group of the alkyne incorporated distal to the phenol group as indicated by the *meta* coupling constant ($J = 3.2$ Hz) exhibited by the aromatic protons of the new benzene ring. The regioselectivity of incorporation of the alkyne appears to be under electronic control. With electron deficient unsymmetrical alkynes, steric effects exert a moderate to strong preference for the installation of the more hindered group *ortho* to the phenolic hydroxyl group. For example, methyl propiolate provided the catechol that



Scheme 2. Addition reaction of dimethylacetylene dicarboxylate with vinylketene, **1**.

Table 1. Catechol synthesis from reaction of vinylketene complex,**2**, with alkynes[a]



2 **3** **4** **5**

Entry	R^1	R^2	Yield (%)	Regioisomeric ratio **4**:**5**
1	H	OEt	35	0:100 (**5a**)
2	H	COOMe	44	100:trace (**4b**)
3	Me	COOMe	67	64:36 (**4c**, **5c**)
4	Me	COOEt	92	30:70 (**4d**, **5d**)
5	Et	COMe	54	43:57 (**4e**)
6	COOMe	COOMe	65	(**4f**)

[a] Reaction conditions: vinylketene complex, **2** (0.5–2.0 mmol) alkyne (7–20 mmol) in THF: (5–20 mL). Reaction time: reflux 24–48 h.

resulted from incorporation of the ester group in the proximal position to the phenol as manifested by the presence of a peak in the ^{1}H NMR at 10.92 ppm. With butynoates and 3-hexyn-2-one the regioselectivity is small and appears to be the result of a delicate balance between steric and electronic factors. The yields of phenols represent purified material and were not determined by direct analysis of the crude product mixtures, which exhibited poorly resolved NMR spectra.

Those alkynes, which failed to produce isolable quantities of phenol included hexyne, phenylacetylene, trimethylsilylacetylene, bis-trimethylsilylacetylene, hexafluorobutyne, and cyclopropylacetylene.[14] In these cases, complex mixtures were obtained, the alkyne trimers were detected by GC–MS and were the major products observed. Detectable quantities of compounds with the molecular weight expected for the phenols were observed in the GC–MS, however efforts to isolate the purified compounds were unsuccessful. It is conceivable that η^3-allyl-η^1-vinylacyl compounds were formed and converted to the desired phenols on the injection block of the GC.

We have discovered that reducing the steric congestion at atom 5 of the oxapentatriene (C-4 of the vinylketene) iron complexes, and activation by substitution with an ethoxy group at atom 3 of the oxapentatriene allows for the synthesis of highly substituted catechol monoethers suitable for elaboration to more complex compounds. Acetylenic ketones, esters, and ethers were all converted to catechols upon reaction with **2**. We are actively exploring improved conditions for the practical development of these reactions through which highly complex aromatic compounds may be synthesized from simple non-aromatic precursors.[16]

Acknowledgments

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2005.11.140.

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15. A Schlenk flask was charged with a solution of 1-bromophenylethene (2.75 g; 15.0 mmol) in anhydrous THF (50.0 mL). The solution was degassed and cooled to −78 °C. A solution of 2.5 M *n*-butyllithium in hexanes (6.60 mL; 16.5 mmol) was added over 10 min and the reaction mixture stirred at −78 °C for 1 h. Freshly distilled $Fe(CO)_5$ (1.98 mL; 15.1 mmol) was then added and the reaction mixture allowed to warm to 0 °C over 2 h. HMPA (17 mL) was then added and the solution cooled to −78 °C. Triethyloxonium tetrafluoroborate (4.3 g; 22.6 mmol) was then added under a strong flow of argon. The mixture was allowed to warm to room temperature over 4 h and diethyl ether added. The mixture was treated with saturated sodium bicarbonate and the organic layer separated. The organic layer was washed with brine and then water and dried over anhydrous sodium sulfate. The residue was filtered through celite and concentrated and subjected to flash column chromatography under argon. A gradient of hexane to 5% ethyl acetate/hexane was employed as the eluent. An orange band was collected and concentrated. Spectral and analytical data for tricarbonyl[2-ethoxy-3-phenylbuta-1,3-diene-1-one iron(0) **2**. (Orange solid). Yield: 46%. ^{1}H NMR (400 MHz, d_6-acetone) δ: 7.76–7.74 (2H, d, $J = 2.8$ Hz, *ortho* CH), 7.46 (3H, t, $J = 7.6$ Hz, *meta* and *para* CH), 4.18 (1H, dq-diastereotopic H, $J = 7.6$, 2.8 Hz), 3.94 (1H, dq, $J = 7.6$, 2.8 Hz diastereotopic H), 2.87 (1H, d, $J = 3.2$ Hz, CH), 1.30 (3H, t, $J = 6.8$ Hz, CH_3), 1.07 (1H, d, $J = 2.4$ Hz, CH). ^{13}C NMR (100 MHz, d_6-acetone) δ: 234.9, 200 (broad), 133.4, 130.5, 130.2, 128.2, 106.7, 99.0, 66.1, 30.5,15.1. IR ($CHCl_3$) 2060, 2000 [vs, $Fe(CO)_3$], 1745 (s, C=O) cm^{-1}.
16. General cycloaddition procedure: A Schlenk tube was charged with 0.5–1.0 mmol of vinylketene complex, which was dissolved in 5.0–10.0 mL anhydrous THF and the solution degassed. Alkyne (3.5–7.0 mmol) was added and the solution heated at reflux under nitrogen for 24–48 h. The solvent was removed and the residue purified through flash column chromatography on silica gel.

1-ethoxyethyne: Spectral and analytical data for (2,5-diethoxybiphenyl-3-ol), **5a** (yellow oil). Yield: 35%. ^{1}H NMR (400 MHz, d_6-benzene) δ 7.65 (2H, d, $J = 8$ Hz, aryl), 7.21 (2H, t, $J = 8$ Hz, aryl), 7.12 (1H, t, $J = 7.9$ Hz, aryl), 6.81 (1H, d, $J = 3.2$ Hz, CH), 6.60 (1H, d, $J = 3$ Hz, CH), 6.05 (1H, s, OH), 3.56 (2H, q, $J = 6.8$ Hz, CH_2CH_3), 3.31 (2H, q, $J = 6.8$ Hz, CH_2CH_3), 1.08 (3H, t, $J = 6.8$ Hz, CH_3), 0.72 (3H, t, $J = 6.8$ Hz, CH_3). ^{13}C NMR (100 MHz, d_6-benzene) δ: 156.5, 151.0, 138.9, 137.4, 135.1, 129.1, 128.6, 127.6, 108.0, 101.1, 69.1, 63.4, 15.1, 14.7. IR (cm^{-1}) 3507 (vbr, O–H), 2978 (s, C=C), 2930 (w, C=C): GC–MS m/z 258 (M^+, 78), 229 (88), 201 (100), 183 (20), 171 (9), 155 (14), 127 (10), 115 (12), 69 (11). *Methyl propynoate*: Spectral and analytical data for (2-ethoxy-3-hydroxybiphenyl-4-carboxylic acid methyl ester), **4b** (yellow oil). Yield: 44%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.92 (1H, s, OH), 7.56 (2H, d, $J = 8.0$ Hz, aryl), 7.53 (1H, d, $J = 6.8$ Hz, aryl), 7.37 (2H, t, $J = 7.6$ Hz, aryl), 7.30 (1H, t, $J = 7.2$ Hz, aryl), 6.82 (1H, d, $J = 8.8$ Hz, aryl), 3.91 (3H, s, OCH_3), 3.76 (2H, q, $J = 6.4$ Hz, CH_2CH_3), 1.07 (3H, t, $J = 6.4$ Hz, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.9, 156.2, 141.9, 137.7, 130.2, 129.4, 128.5, 128.1, 124.6, 120.3, 121.5, 68.9, 52.4, 15.7. IR (cm^{-1}) (w, OH), 2960 (w, C=C), 2800 (C–C), 1794 (w, C=O): MS m/z 272 (M^+, 93), 239 (100), 225 (15), 211 (75), 197 (29), 184 (43), 168 (11) 155 (25), 139 (11), 127 (29), 53 (16). *Methyl butynoate*: Spectral and analytical data for (2-ethoxy-3-hydroxy-5-methyl-biphenyl-4-carboxylic acid methyl ester), **4c** (yellow oil). Yield: 43%. ^{1}H NMR (400 MHz, d_6-benzene): δ 12.06 (1H, s, OH), 7.67 (2H, dd, $J = 8$ Hz, aryl), 7.242 (2H, t, $J = 7.2$ Hz, aryl), 7.17 (1H, t, $J = 7.2$ Hz, aryl), 6.68 (1H, s, CH), 3.94 (2H, q, $J = 8.0$ Hz, OCH_2CH_3), 3.26 (3H, s, OCH_3), 2.34 (3H, s, CH_3), 1.10 (3H, t, $J = 7.2$ Hz, OCH_2CH_3). ^{13}C NMR (100 MHz, d_6-benzene): δ 172.3, 157.9, 140.3, 138.2, 135.1, 129.6, 129.2, 128.1, 123.6, 112.4, 68.4, 51.4, 30.0, 23.6, 15.6. IR (cm^{-1}) 3400 (w, OH), 2927 (s, C=C) 1731 (w, C=O): MS m/z 286 (M^+, 57), 253 (100) 239 (26), 225 (55), 211 (23), 197 (48), 141 (22), 115 (16), 67 (17). Spectral and analytical data for (6-ethoxy-5-hydroxy-4-methylbiphenyl-3-carboxylic acid methyl ester), **5c** (yellow oil). Yield: 24%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (2H, dd, $J = 7.2$ Hz, aryl), 7.41 (s, 1H, aryl), 7.35 (2H, t, $J = 8.0$ Hz, aryl), 7.28 (1H, t, $J = 7.6$ Hz, aryl), 6.17 (1H, s, OH), 3.80 (3H, s, OCH_3), 3.52 (2H, q, $J = 6.4$ Hz, OCH_2CH_3), 2.46 (3H, s, CH_3), 1.08 (3H, t, $J = 6.8$ Hz, OCH_2CH_3). ^{13}C NMR (100 MHz, d_6-benzene): δ 167.4, 148.7, 145.7, 138.1, 130.9, 128.8, 128.6, 126.9, 126.5, 124.5, 124.4, 69.0, 51.3, 15.0, 13.4. IR (cm^{-1}) 3503 (br, OH), 2951 (w, C=C), 1719 (s, C=O): MS m/z 286 (M^+, 100), 258 (31), 227 (56), 198 (50), 141 (19), 115 (14). *Ethyl butynoate:* Spectral and analytical data for (2-ethoxy-3-hydroxy-5-methylbiphenyl-4-carboxylic acid ethyl ester), **4d** (red-brown oil). Yield: 28%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 11.48 (1H, s, OH), 7.54 (2H, d, $J = 9.0$ Hz, aryl), 7.37 (2H, t, $J = 9.0$ Hz, aryl) 7.31 (1H, t, $J = 9.0$ Hz, aryl), 6.66 (1H, s, CH), 4.39 (2H, q, $J = 9.0$ Hz, $O_2CH_2CH_3$), 3.71 (2H, q, $J = 9.0$ Hz, OCH_2CH_3), 2.48 (3H, s, CH_3), 1.38 (3H, t, $J = 9.0$ Hz, OCH_2CH_3), 1.06 (3H, t, $J = 9.5$ Hz, $O_2CH_2CH_3$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.9 157.1, 140.0, 137.7, 135.7, 129.4, 128.3, 127.9, 123.7, 112.5, 68.8, 61.9, 29.9, 24.1, 15.7, 14.4. IR 2929 (br, C=CH), 1733 (C=O): MS m/z 300 (M^+, 83), 272 (9), 253 (100), 239 (26), 226 (60), 211 (23), 197 (49), 141 (29), 115 (23), 67 (18). Spectral and analytical data for (6-ethoxy-5-hydroxy-4-methylbiphenyl-3-carboxylic acid ethyl ester), **5d** (red-brown oil). Yield: 64%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.58 (2H, d, $J = 8.0$ Hz, aryl,), 7.46 (1H, s, CH), 7.44 (2H, t, $J = 8.0$ Hz, aryl),7.36 (1H, t, $J = 7.0$, aryl), 6.23 (1H, s, OH), 4.35 (2H, q, $J = 7.2$ Hz, $O_2CH_2CH_3$), 3.59 (2H, q, $J = 6.8$ Hz, OCH_2CH_3), 2.53 (3H, s, CH_3), 1.38 (3H, t, $J = 7.2$ Hz, OCH_2CH_3), 1.156 (3H, t, $J = 6.8$ Hz, $O_2CH_2CH_3$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.8, 148.3, 137.8, 130.9, 128.8, 128.7, 127.8, 127.0, 125.8, 124.0, 123.9, 69.4, 61.0, 12.7, 14.6, 3.3. IR (cm^{-1}) 3507 (br, OH), 2979 (C=CH), 2934 (C–C), 1716 (s, C=O): MS m/z 300 (M^+, 100), 272 (23), 255 (23), 255 (29), 243 (17), 226 (48), 199 (28), 181 (14), 115 (14). *3-Hexyn-2-one*: Spectral and analytical data for {1-(2-ethoxy-5-ethyl-3-hydroxybiphenyl-4-yl)-ethanone}, **4e** (yellow crystalline solid). Yield: 23%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (2H, d, $J = 8$ Hz, aryl CH), 7.45 (2H, t, $J = 7.4$ Hz, aryl CH), 7.31 (t, 1H, $J = 7.4$ Hz, aryl), 7.10 (1H, s, PhH), 6.19 (1H, s, OH), 3.59 (2H, q, $J = 7.2$ Hz, OCH_2CH_3), 2.83 (2H, q, $J = 7.2$ Hz, CH_2CH_3), 2.57 (3H, s, $COCH_3$), 1.24 (3H, t, $J = 7.2$ Hz, OCH_2CH_3), 1.16 (3H, t, $J = 7.2$ Hz, CH_2CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.6, 148.0, 145.1, 137.5, 134.8, 130.6, 130.0, 128.6, 127.6, 122.5, 122.6, 69.3, 30.0, 20.3, 15.5, 14.4. IR (cm^{-1}) 3358 (vbr, OH), 2966 (w, C=C), 2934 (w, C–C), 1678 (vs, C=O). MS m/z 284 (M^+, 100), 269 (26), 255 (60), 241 (68), 223 (15), 165 (20), 152 (12). Spectral and analytical data for {1-(6-ethoxy-4-ethyl-5-hydroxybiphenyl-3-yl)-ethanone}, **5e** (yellow crystalline solid). Yield: 31%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (1H, s, PhH), 7.58 (1H, d, $J = 7.2$ Hz, aryl H(*ortho*)), 7.44 (2H, t, $J = 7.2$ Hz, aryl H(*meta*)), 7.38 (1H, t, $J = 7.2$ Hz, aryl(*para*)), 6.77 (1H, s, OH), 3.61 (2H, q, $J = 7.2$ Hz, OCH_2CH_3), 2.71 (2H, q, CH_2CH_3), 2.65 (3H, s, CH_3), 1.24 (3H, t, $J = 7.2$ Hz, OCH_2CH_3), 1.14 (3H, t, $J = 7.2$ Hz, CH_2CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 204.8, 149.3, 141.8, 138.4, 137.8, 136.5, 128.6, 128.0, 125.7, 122.4, 69.3, 32.6, 29.9, 26.9, 16.4, 15.7. IR (cm^{-1}) 3375 (br, OH), 2975 (w, C=C), 2929 (vw, C–C), 1691 (vs, C=O). MS m/z 284 (M^+, 73), 269 (59), 241 (100), 165 (10), 152 (8), 128 (6). *Dimethyl acetylene dicarboxylate*: Spectral and analytical data for (6-ethoxy-5-hydroxybiphenyl-3,4-dicarboxylic acid dimethyl ester), **4f** (yellow oil). Yield: 65%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.75 (1H, s, OH) 7.54 (1H, dd, $J = 7.8$; 1.7 Hz, aryl C–H), 7.39 (3H, m, $J = 7.5$ Hz; 1.8 Hz, aryl C–H), 7.13 (s, aryl C–H), 3.93 (3H, s, OCH_3), 3.86 (3H, s, OCH_3), 3.78 (2H, q, $J = 7.1$ Hz, CH_2), 1.12 (3H, t, $J = 7.1$ Hz, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.8, 167.0, 153.5, 146.6, 138.9, 136.6, 129.0, 128.3, 121.6, 69.1, 52.9, 52.6, 15.4. IR (cm^{-1}) 3500 (w, OH), 2980 (w, C=C), 1720 (w, C=O), 1435 (w, O–C). MS m/z 330 (15, M^+), 283 (40), 196 (45), 126 (35), 77 (15).