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A [3.3]Sigmatropic Rearrangement of α,β-Unsaturated Fischer Chromium Carbenes: Synthesis of Alkynol and Dienol Esters

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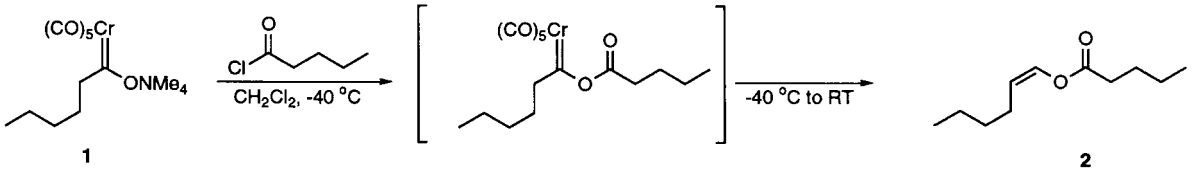
Abstract—A novel [3.3]sigmatropic rearrangement of in situ formed α,β-unsaturated Fischer acyloxy carbenes forming alkynol esters is described. For example, reaction of tetramethylammonium pentacarbonyl(1-oxo-2-butenyl)chromate(1-) (**4**) with 4-methoxybenzoyl chloride gave 2-methyl-3-butyn-2-yl 4-methoxybenzoate (**8**) in 32% yield. In addition to the rearrangement products, dienol esters formed by a formal β-hydride elimination-reductive elimination sequence were usually isolated. In the above example, 3-methylbuta-1,3-dien-1-yl 4-methoxybenzoate (**9**) was obtained (16%) as the side product.

Carbonyl(1-oxoalkyl)metalate(1-) salts, e.g., those of chromium, molybdenum, tungsten, manganese, and iron, have been extensively used as precursors to alkoxy and amino substituted Fischer carbenes. For example, alkoxy chromium carbenes are usually formed by alkylation of lithium pentacarbonyl(1-oxoalkyl)chromate(1-) complexes with highly reactive alkylating reagents such as Meerwein reagents or alkyl iodides, or by reaction of the corresponding tetramethylammonium pentacarbonyl(1-oxoalkyl)chromate(1-) complexes with acyl halides followed by nucleophilic substitution of the formed acyloxy carbene, employing the appropriate alcohol. The formed chromium and molybdenum 1-acyloxy substituted Fischer carbenes are, in comparison to the alkoxy and amino substituted carbenes, relatively unstable and rapidly decompose at room temperature. Their tungsten counterparts are somewhat more stable but undergo decomposition when heated at 50°C.[2,3]

Apart from their use as intermediates in the synthesis of alkoxy and amino substituted carbenes, only a handful of reactions of acyloxy carbene complexes have been published.[4] We have recently developed a synthesis of *Z*-enol esters via in situ formed acyloxy substituted Fischer chromium carbene complexes.[5] For example, acylation of tetramethylammonium pentacarbonyl(1-oxohexyl)chromate(1-) (**1**) with pentanoyl chloride at −40°C, followed by slow warming to ambient temperature, gave (*Z*)-1-hexen-1-yl pentanoate (**2**) in 82% isolated yield (Scheme 1). The *Z*/*E* ratio was found to be in excess of 20:1.

Related elimination reactions forming enol ethers,[6] dihydrofurans,[7] tetrahydropyrans,[8] imines,[9] ene carbamates,[10] vinylsilanes,[11] and alkenes[12] have been reported for alkoxy and amino substituted Fischer chromium carbenes. These reactions are usually performed under thermal conditions in the presence of an amine base, affording the *Z*-isomer as the predominant product.[13]

Dixneuf et al. have also developed a route to enol esters consisting of a ruthenium-catalyzed addition of carboxylic acids to terminal alkynes.[14] High selectivity for the *Z*-enol ester was generally observed. For example, addition of benzoic acid to 1-hexyne produced enol ester **3** in 95% yield with a 98% selectivity for the *Z*-isomer.[15] Although the two reactions depicted in Schemes 1 and 2 have different



1 2

Scheme 1.

Keywords: rearrangements; carbenes; alkynes.

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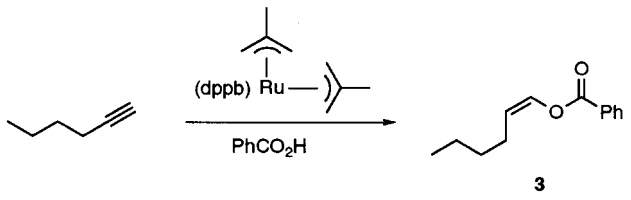


Scheme 2.

starting materials, they are probably mechanistically related. In the ruthenium-catalyzed case, an alkyne-vinylidene isomerization followed by addition of an acid would afford a σ-bonded enol ester intermediate (Scheme 3). The same type of intermediate can be formed by a formal β-hydride elimination from the acyloxy carbene complex. Protonation of the metal, followed by reductive elimination or protonolysis of the metal-carbon σ-bond, would give the observed products.

As a logical extension of the reaction forming enol esters, we initiated a study of the reaction of α,β-unsaturated Fischer carbene complexes with acid halides, anticipating the formation of dienol esters. A similar extension of the ruthenium-catalyzed reaction has been reported.[16] In our initial reaction, treatment of tetramethylammonium complex **4** with 4-methoxybenzoyl chloride at −40°C, followed by slow warming to ambient temperature, gave a small amount of the expected diene **9** (16%, *Z*/*E*=4:1, Scheme 4). The main product was identified as the alkynol ester **8**, isolated in 32% yield. Independent synthesis of **8** using 3-butyn-2-ol and 4-methoxybenzoyl chloride confirmed the proposed structure. This is to our knowledge a novel reaction of Fischer carbenes. Herein is reported a study of the scope and limitations of the formation of alkynol/dienol ester from α,β-unsaturated Fischer carbenes.

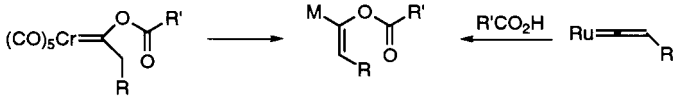
Results and Discussion

To evaluate the generality of the reaction shown in Scheme 4, four tetramethylammonium pentacarbonyl(1-oxo-2-alkenyl)chromate(1-) complexes were prepared according to standard procedures. Thus, addition of the appropriate vinyllithium reagent to chromium hexacarbonyl, followed by exchange of the cation using tetramethylammonium bromide, gave complexes **4**–**7** in good isolated yields. The complexes were isolated as red–brown solids that slowly decompose at ambient temperature. The anionic carbene complexes were reacted with a number of carboxylic acid chlorides, and the results of these experiments are summarized in Table 1.

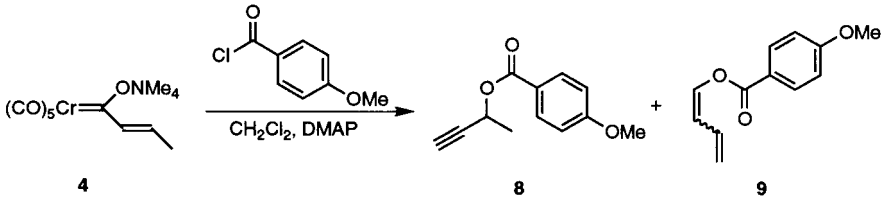
The first few experiments were performed in the presence of a base, *N*,*N*-4-dimethylaminopyridine, conditions previously shown to improve the yield of enol esters. However, little or no beneficial effect of added base was observed in the case of α,β-unsaturated Fischer carbenes. The initial reaction temperature was shown to substantially influence the ratio of alkynol to dienol ester. For example, addition of 4-methoxybenzoyl chloride to a solution of complex **4**, either at −40°C or at ambient temperature, drastically changed the ratio of **8** and **9** from 2:1 to 1:2, respectively (entries 1–2). It should be noted that the combined yield of products remained within the experimental error for the two reactions. Addition of the acid chloride at a lower temperature (−78°C) did not significantly change the yield. This can probably be explained by the observation that no visible reaction between the carbene and the acid halide occurred until the temperature of the solution reached ca. −45°C. A noticable change in color to dark red–brown was observed between −45°C and −35°C. Similar results were obtained using carbene **5** (entry 3). It should be noted that all dienol esters reported herein are unstable, and readily decompose upon standing at ambient temperature. IR, ^{1}H NMR, ^{13}C NMR, and GC–MS (EI) spectra all corroborate the assigned structure however, only for dienol esters **13** and **23** were we able to obtain satisfactory elemental analyses.

The effect of solvent was briefly examined, and results similar to those previously reported for the synthesis of enol esters were obtained. Dichloromethane proved to be a superior solvent compared to tetrahydrofuran and hexanes, and a similar yield of alkynol ester was obtained using acetonitrile (entries 4–7).

The electronic properties of the acid chloride were shown to have a significant effect on the outcome of the reaction. As a general trend, aroyl chlorides having an electron donating group in the para position, relative to the acid moiety, gave a higher yield of alkynol esters. For example, reaction of

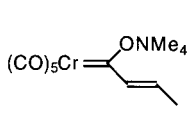
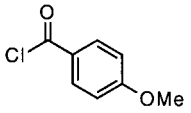
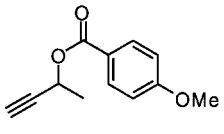
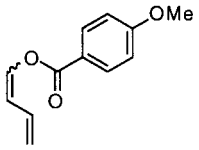
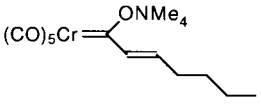
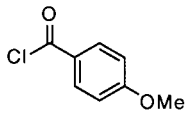
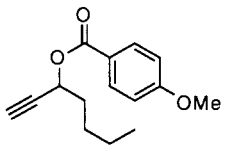
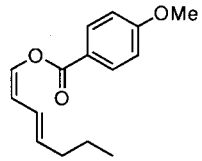
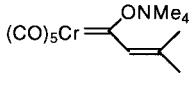
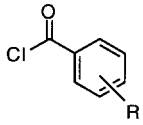
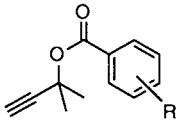
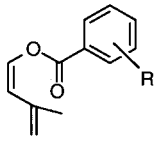
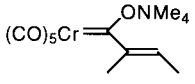
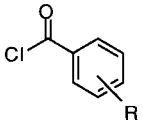
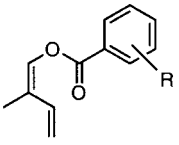


Scheme 3.



Scheme 4.

Table 1. Alkynol and dienol esters from anionic α,β -unsaturated fischer carbenes

Entry	Complex[a]	Acid Chloride	Products (Yield)[b]	
				
1	**4**		**8** (32%)	**9** (16%)[c]
2	**4** (RT)		**8** (22%)	**9** (32%)[c]
				
3	**5**		**10** (22%)	**11** (8%)[d]
				
4	**6**	R = 4-OMe	**12** (45%)	**13**(19%)[e]
5	**6** (hexanes)	R = 4-OMe	**12** (12%)	
6	**6** (THF)	R = 4-OMe	**12** (6%)	**13** (11%)[e]
7	**6** (MeCN)	R = 4-OMe	**12** (41%)	**13** (4%)[e]
8	**6**	R = 2,4-diOMe	**14** (40%)	
9	**6**	R = 3-OMe	**15** (25%)	**16** (17%)[f]
10	**6**	R = H	**17** (28%)	**18** (5%)[g]
11	**6**	R = 4-NO_2	**19** (9%)	**20** (2%)[h]
				
12	**7**	R = 4-OMe		**21** (70%)[i]
13	**7**	R = 3-OMe		**22** (74%)[j]
14	**7**	R = 4-NO_2		**23** (33%)[k]

[a] For typical reaction conditions, see Experimental.
[b] Isolated yields of pure products.
[c] *Cis–trans*=4:1.
[d] Isomer ratio=2:2:1:1.
[e] *Cis–trans*>20:1.
[f] *Cis–trans*=10:1.
[g] *Cis–trans*>20:1.
[h] Tentatively assigned based on ^{1}H NMR.
[i] *Cis–trans*=5:3:1.
[j] *Cis–trans*=3:8:1.
[k] *Cis–trans*=4.6:1.

4-methoxy, 3-methoxy, unsubstituted, and 4-nitrobenzoyl chloride with complex **6**, gave alkynol esters in 45%, 25%, 28%, and 9% yield, respectively (entries 4, 9–11). The combined yield of ester products also rapidly decreased with decreasing electron donating ability. An additional electron donating methoxy group does not appear to improve the yield of alkynol ester; however, no dienol ester was isolated using 2,4-dimethoxybenzoyl chloride (entry 8). From the results shown in Table 1, it is suggested that the electron donating group must be in conjugation with

the carbonyl group, allowing for an increase in electron density on the carbonyl oxygen. Adding electron density to the aromatic ring is alone not sufficient; for example, no added benefit was seen when 3-methoxybenzoyl chloride was used compared to the unsubstituted benzoyl chloride (entries 9–10). Finally, acetyl chloride and benzyl chloroformate were reacted with complex **6**; however, no product was obtained in either case.

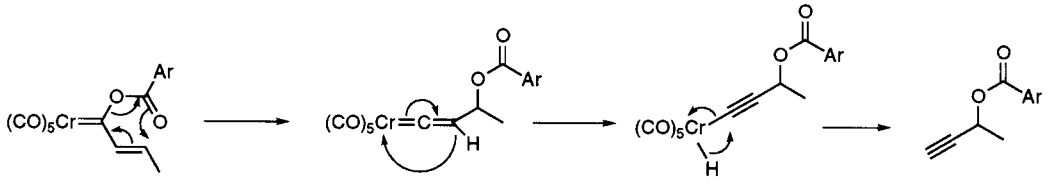
Complexes having a substituent in the α-position can for obvious reasons not form alkynol esters. Reaction of complex **7**, with carboxylic acid halides, affords dienol esters in good yields using electron-rich aromatic acid halides, regardless of the position of the methoxy group (entries 12–13). In contrast, a substantially lower yield was obtained using 4-nitrobenzoyl chloride (entry 14).

The stereochemistry and ratio of isomers of the dienol esters were deduced from their ^{1}H NMR spectra. Relatively small H–H coupling constants, J=6.2–7.3 Hz, were observed across the OCH=CH double bond of the major product, typical for a *Z*-configuration. Corresponding coupling constants for the *E*-isomers ranged from 11.9 to 12.1 Hz. In addition, the methyl resonance shifts about 0.4 ppm downfield for the *Z*-relative to the *E*-isomers. The stereochemistry of the trisubstituted esters **21**–**23** was assigned using the chemical shift of the C*H*–O and the methyl protons. The C*H*–O proton resonates for the *E*-isomers at δ 7.27 ppm and for the *Z*-isomers at δ 7.50–7.51 ppm, and the singlet for the methyl group resonates at 0.07–0.12 ppm upfield for the *E*-compared to the *Z*-isomers. Similar upfield shifts, for C*H*–O protons, have previously been reported for related enol esters. In addition, the resonance for the methyl group of the minor *E*-isomer shifts 0.07–0.12 ppm upfield compared to the *Z*-isomer.[17]

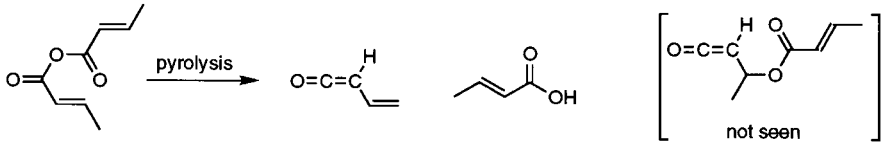
A possible mechanism involving an electrocyclic rearrangement is depicted in Scheme 5. A formal [3,3]sigmatropic rearrangement producing a vinylidene complex, followed by a 1,3-hydride shift and reductive elimination, would furnish the observed alkynol esters. We have presently no evidence that the reaction is concerted; thus a step-wise process cannot be ruled out. The 1,3-hydride shift-reductive elimination sequence is the reverse of the mechanism proposed for a number of reactions of low valent metal carbonyl complexes with alkynes and alkynols leading to Fischer carbene complexes, furan derivatives, and lactones.[18]

Thermal reaction of the isolobal α,β-unsaturated anhydride, 2-butenoic acid anhydride (Scheme 6) has been reported previously.[19] Upon pyrolysis at 550°C (0.1 Torr), vinyl ketene was isolated and characterized at low temperature. Considering the high pyrolysis temperature used, it is not unlikely that a ketene related to the vinylidene chromium complex (Scheme 5) is formed as an intermediate followed by elimination of butenoic acid. In order to compare the two reactions, complex **4** was reacted with 2-butenoyl chloride; however, no rearrangement product was observed.

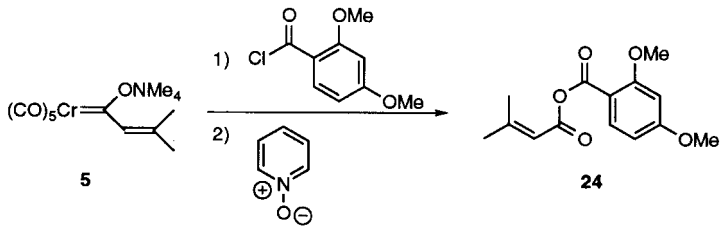
In addition to the esters discussed above, minor amounts (0–2%) of mixed anhydrides were isolated in some cases. These products are probably formed by oxidation of the acylated Fischer carbenes with oxygen present in the solvent. In order to verify the identity of the anhydrides, complex **6** was reacted with 2,4-dimethoxybenzoyl chloride at −40°C.



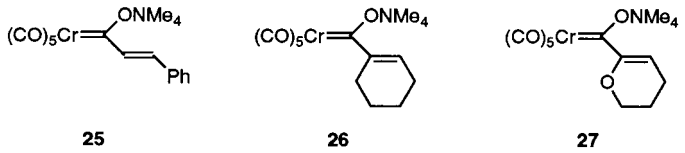
Scheme 5.



Scheme 6.



Scheme 7.



25 26 27

Figure 1.

After 1 h at −40°C, 2 equiv. of pyridine *N*-oxide was added, and the reaction mixture was allowed to slowly reach ambient temperature. Purification by chromatography gave **24** in 64% yield (Scheme 7), identical to the minor product obtained from reaction of **6** with 2,4-dimethoxybenzoyl chloride. Dimethyl sulfoxide is also known to oxidize Fischer carbene complexes to the corresponding carbonyl compound. In our case, oxidation of the acylated carbene using DMSO as the oxidant gave **24** in only 13% yield.

Finally, synthesis of some additional carbenes was attempted, for example the styryl carbene **25**, the tetrahydropyran carbene **26**, and the cyclohexenyl carbene **27**; however, low yields of impure materials were obtained in all cases (Fig. 1). Reaction of the crude carbenes with benzoyl chlorides gave little or none of the expected product. We have presently no explanation for this observation.

In conclusion, a novel [3.3]sigmatropic rearrangement of α,β-unsaturated acyloxy Fischer chromium carbenes has been examined. Moderate yields of alkynol esters can be obtained using alkoxy substituted benzoyl chlorides. In addition, dienol esters were isolated as minor products in most of the reaction. Dienol esters were obtained in good yields when the rearrangement was blocked by an α-methyl group.

Experimental

General procedures

All NMR spectra were determined in $CDCl_3$ at 270 MHz (^{1}H NMR) and 67.5 MHz (^{13}C NMR) unless otherwise stated. The chemical shifts are expressed in δ values relative to Me_4Si (0.0, ^{1}H and ^{13}C), $CDCl_3$ (77.0, ^{13}C), or DMSO-d_6 (39.5, ^{13}C) internal standards. ^{1}H–^{1}H coupling constants are reported as calculated from spectra; thus, a slight difference between $J_{a,b}$ and $J_{b,a}$ is usually obtained. Results of APT (attached proton test)—^{13}C NMR experiments are shown in parentheses where, relative to $CDCl_3$ or DMSO-d_6, (−) denotes CH_3 or CH and (+) denotes CH_2 or C.

Tetrahydrofuran (THF), 1,4-dioxane, toluene, and diethyl ether were distilled from sodium benzophenone ketyl prior to use. Hexanes, acetonitrile, dichloromethane, and ethyl acetate were distilled from calcium hydride. Chemicals prepared according to literature procedures have been footnoted first time used; all other reagents were obtained from commercial sources and used as received. All reactions were performed in oven dried glassware under an argon atmosphere. Solvents were removed on a rotary evaporator at water aspirator pressure unless otherwise stated. Silica gel (200–400 mesh) was used for chromatography. Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA. High resolution mass spectra were obtained at University of California at Riverside Mass Spectrometry Center.

Tetramethylammonium pentacarbonyl(1-oxo-3-methyl-2-butenyl)chromate(1-) (6). *tert*-Butyllithium (23.5 mL, 40.0 mmol, 1.7 M in pentane) was added to a −78°C cold solution of 1-bromo-2-propene (2.05 mL, 20.0 mmol) in Et_2O (25 mL). After stirring for 30 min at −78°C and 30 min at ambient temperature, the resulting yellow solution was added, via a cannula, to a 0°C cold slurry of chromium hexacarbonyl (4.40 g, 20.0 mmol) in Et_2O (50 mL). The resulting reaction mixture was stirred at 0°C for 30 min then at ambient temperature for 30 min. Removal of the solvents from the dark solution gave an orange–brown residue. To the solid was added a solution of tetramethylammonium bromide (6.16 g, 40.0 mmol) in water (50 mL), and the mixture was stirred vigorously (20 min). CH_2Cl_2 (50 mL) was added, and the phases were separated. The aqueous phase was extracted with CH_2Cl_2 (3×50 mL), and the combined organic phases were dried ($MgSO_4$) and filtered. Solvent removal gave **6** (5.72 g, 16.4 mmol, 82%) as a redish–brown solid. Mp 93–96.5°C; IR (CH_2Cl_2) 2080, 1876 cm^{-1}; ^{1}H NMR δ 6.61 (br s, 1H), 3.47 (br s, 12H), 1.65 (br s, 6H); ^{13}C NMR δ 290.9 (+), 226.7 (+), 221.4 (+), 141.9 (−), 120.1 (+), 54.2 (−), 23.1 (−), 17.2 (−).

Tetramethylammonium pentacarbonyl(1-oxo-2-heptenyl)-chromate(1-) (5). Similar reaction of *E*-1-iodo-1-hexene[20] (540 mg, 2.57 mmol) with, in sequence, *tert*-butyllithium (3.20 mL, 5.14 mmol), chromium hexacarbonyl (566 mg, 2.57 mmol), and tetramethylammonium bromide (792 mg, 5.14 mmol) gave **5** (528 mg, 1.40 mmol, 54%) as a brown solid. Mp 85.5–88°C; IR (CH_2Cl_2) 2034, 1896 cm^{-1}; ^{1}H NMR δ 6.43 (d, J=14.6 Hz, 1H), 5.80 (dt, J=15.4 and 6.2 Hz, 1H), 3.46 (br s, 12H), 2.05 (unresolved q, J=4.0 Hz, 2H), 1.40 (m, 4H), 0.89 (t, J=6.4 Hz, 3H); ^{13}C NMR δ 294.7, 228.2, 222.9, 146.1, 130.7, ca. 61 (br), 31.0, 30.8, 22.0, 13.6.

3-Butyn-2-yl 4-methoxybenzoate (8) and buta-1,3-dien-1-yl 4-methoxybenzoate (9). A slurry of tetramethylammonium pentacarbonyl(1-oxo-2-butenyl)chromate(1-) (**4**)[4a] (260 mg, 0.78 mmol) and 4-*N*,*N*-dimethylaminopyridine (94 mg, 0.77 mmol) in CH_2Cl_2 (25 mL) was cooled to −40°C under argon. 4-Methoxybenzoyl chloride (108 μL, 0.77 mmol) was added via syringe resulting in a rapid color change from orange–red to dark red. The reaction mixture was allowed to slowly reach ambient temperature overnight. The resulting green slurry was filtered through Celite, and the Celite pad was washed with CH_2Cl_2. Removal of the solvent followed by chromatography (hexanes–EtOAc, 19:1), gave **9** (25 mg, 0.12 mmol, 15%) followed by **8** (52 mg, 0.38 mmol, 33%), both

as white solids. Analytical data for **8**: mp 56–57.5°C; IR ($CDCl_3$) 1722 cm^{-1}; ^1H NMR δ 7.98 (d, J=8.9 Hz, 2H), 6.87 (d, J=8.9 Hz, 2H), 5.62 (dq, J=6.7 and 2.2 Hz, 1H), 3.79 (s, 3H), 2.49 (d, J=2.2 Hz, 1H), 1.59 (d, J=6.7 Hz, 3H); ^{13}C NMR δ 164.9 (+), 163.4 (+), 131.6 (−), 121.9 (+), 113.4 (−), 82.2 (+), 72.8 (+), 60.0 (−), 55.2 (−), 21.2 (−); Anal. calcd for $C_{12}H_{12}O_3$: C, 70.59; H, 5.88. Found: C, 70.52; H, 5.94. Analytical data from a 4:1 *Z*/*E* mixture of **9**: IR (neat) 1724, 1264, 793 cm^{-1}; ^1H NMR δ (*Z*) isomer: 8.07 (d, J=8.9 Hz, 2H), 7.29 (d, J=6.5 Hz, 1H), 6.94 (d, J=8.9 Hz, 2H), 6.86 (td, J=17.3 and 6.7 Hz, 1H), 5.60 (dd, J=10.9 and 6.3 Hz, 1H), 5.28 (d, J=16.4 Hz, 1H), 5.14 (d, J=10.7 Hz, 1H), 3.87 (s, 3H); *E* isomer (peaks not obscured by the major isomer): 7.62 (d, J=11.9 Hz, 1H), 6.80 (td, J=17.2 and 6.9 Hz, 1H), 6.21 (q, J=11.7 Hz, 1H); ^{13}C NMR δ 163.9 (+), 163.1 (+), 162.7 (+), 139.1 (−), 134.4 (−), 132.1 (−0, 131.9 (−), 129.0 (−), 121.2 (+), 121.0 (+), 117.6 (+), 117.0 (+), 116.1 (−), 113.9 (−), 113.5 (−), 55.5 (−).

3-Butyn-2-yl 4-methoxybenzoate (8). A solution of 3-butyne-2-ol (391 μL, 5.00 mmol) in pyridine (15 mL) was treated with 4-methoxybenzoyl chloride (703 μL, 5.00 mmol) under an argon atmosphere. After stirring for 18 h, the formed white precipitate was filtered off and washed with dichloromethane. The solvents were removed, and the semi-solid residue was put on top of a silica gel column. Elution of the product using pentane–diethyl ether (9:1) gave **8** (790 mg, 3.87 mmol, 77%) as a white solid.

1-Heptyn-3-yl 4-methoxybenzoate (10) and 1,3-heptadien-1-yl 4-methoxybenzoate (11). Reaction of **5** (377 mg, 1.00 mmol) in CH_2Cl_2 (25 mL) with 4-methoxybenzoyl chloride (136 μL, 1.00 mmol) gave, after chromatography (hexanes–EtOAc, 9:1), **11** (20 mg, 0.08 mmol, 8%) followed by **10** (55 mg, 0.22 mmol, 22%) both as colorless oils. Analytical data for **10**: IR (neat) 1717, 1605, 1256 cm^{-1}; ^1H NMR δ 8.02 (d, J=8.6 Hz, 2H), 6.92 (d, J=8.6 Hz, 2H), 5.58 (dt, J=6.7 and 2.0 Hz, 1H), 3.86 (s, 3H), 2.48 (d, J=2.2 Hz, 1H), 1.91 (m, 2H), 1.57–1.32 (m, 4H), 0.99 (t, J=7.2 Hz, 3H); ^{13}C NMR δ 165.2 (+), 163.5 (+), 131.8 (−), 122.2 (+), 113.6 (−), 81.5 (+), 73.4 (+), 63.9 (−), 55.4 (−), 34.4 (+), 27.1 (+), 22.2 (+), 13.9 (−); GC-MS (EI) *m*/*z* 246 (M^+), 135 ($ArC{=}O^+$). Analytical data from a 2:2:1:1 (*Z*:*Z*:*E*:*E*) isomer mixture of **11**: IR (CH_2Cl_2) 1719, 1256 cm^{-1}; ^1H NMR δ 8.11–8.02 (m), 7.60 (d J=12.1 Hz), 7.53 (d, J=11.9 Hz), 7.31 (d, J=6.4 Hz), 7.19 (d, J=6.2 Hz), 6.98–6.92 (m), 6.58–5.48 (m), 3.88 (s), 3.87 (s), 3.86 (s), 3.85 (s), 2.23–2.05 (m), 1.53–1.40 (m), 0.94 (t, J=7.2 Hz).

2-Methyl-3-butyn-2-yl 4-methoxybenzoate (12) and 3-methylbuta-1,3-dien-1-yl 4-methoxybenzoate (13). Reaction of **6** (349 mg, 1.00 mmol) and 4-*N*,*N*-dimethylaminopyridine (122 mg, 1.00 mmol) in CH_2Cl_2 (25 mL) with 4-methoxybenzoyl chloride (141 μL, 1.00 mmol) as described above gave, after chromatography (hexanes–EtOAc, 9:1), **13** (41 mg, 0.19 mmol, 19%) followed by **12** (97 mg, 0.44 mmol, 44%) both as white solids. Spectral data for **12**: mp 34–35°C; IR (neat) 1725 cm^{-1}; ^1H NMR δ 7.95 (d, J=8.9 Hz, 2H), 6.88 (d, J=9.1 Hz, 2H), 3.83 (s, 3H), 2.50 (s, 1H), 1.81 (s, 6H); ^{13}C NMR δ 164.6 (+), 163.3 (+), 131.6 (−), 123.1 (+), 113.4 (−), 84.9 (+), 72.3 (+), 71.8 (+), 55.4 (−), 29.0 (−); Anal. calcd for $C_{13}H_{14}O_3$: C, 71.51; H, 6.48. Found: C, 71.39; H, 6.56. Spectral data for **13**: mp 55–56°C; IR (neat) 1736 cm^{-1}; ^1H NMR δ 8.03 (d, J=9.1 Hz, 2H), 7.24 (d, J=7.1 Hz, 1H), 6.94 (d, J=8.9 Hz, 2H), 5.44 (d, J=7.3 Hz, 1H), 5.07 (br s, 1H), 4.96 (br s, 1H), 3.86 (s, 3H), 2.17 (s, 3H); ^{13}C NMR δ 163.9 (+), 163.1 (+), 139.2 (+), 133.2 (−), 132.0 (−), 121.1 (+), 117.4 (+), 114.4 (−), 113.9 (−), 55.5 (−), 22.9 (−); Anal. calcd for $C_{13}H_{14}O_3$: C, 71.51; H, 6.48. Found, C, 71.25; H, 6.61.

2-Methyl-3-butyn-2-yl 2,4-dimethoxybenzoate (14). Reaction of **6** (700 mg, 2.00 mmol) in CH_2Cl_2 (30 mL) with 2,4-dimethoxybenzoyl chloride (401 mg, 2.00 mmol) as described above (24.5 h) gave, after chromatography (pentane–Et_2O, 1:1), **14** (199 mg, 0.80 mmol, 40%) as off-white crystals. Mp 75–77°C; IR ($CDCl_3$) 2222, 1726 cm^{-1}; ^1H NMR δ 7.87 (d, J=9.3 Hz, 1H), 6.48 (dd, J=7.1 and 2.2 Hz, 2H), 3.87 (s, 3H), 3.85 (s, 3H), 2.55 (s, 1H), 1.80 (s, 6H); ^{13}C NMR δ 164.3 (+), 163.6 (+), 161.9 (+), 134.1 (−), 112.6 (+), 104.5 (−), 98.9 (−), 85.2 (+), 72.2 (+), 71.6 (+), 55.9 (−), 55.5 (−), 29.2 (−); Anal. calcd for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50. Found: C, 67.66; H, 6.62.

2-Methyl-3-butyn-2-yl 3-methoxybenzoate (15) and 3-methylbuta-1,3-dien-1-yl 3-methoxybenzoate (16). Reaction of **6** (1.40 g, 4.00 mmol) in CH_2Cl_2 (50 mL) with 3-methoxybenzoyl chloride (560 μL, 4.00 mmol) as described above (20.5 h) gave, after chromatography (pentane–Et_2O, 9:1), **16** (142 mg, 0.67 mmol, 17%) followed by **15** (217 mg, 1.00 mmol, 25%) both as colorless oils. Analytical data for **15**: IR (neat) 3290, 1724, 1288 cm^{-1}; ^1H NMR δ 7.61 (d, J=7.7 Hz, 1H), 7.56 (d, J=1.5 Hz, 1H), 7.33 (t, J=7.9 Hz, 1H), 7.09 (dd, J=8.2 and 7.5 Hz, 1H), 3.85 (s, 3H), 2.59 (s, 1H), 1.82 (s, 6H); ^{13}C NMR δ 164.6 (+), 159.5 (+), 132.1 (+), 129.2 (−), 121.9 (−), 119.3 (−), 114.1 (−), 84.6 (+), 72.5 (+), 72.3 (+), 55.4 (−), 29.0 (−); Anal. calcd for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47. Found: C, 71.32; H, 6.56. Analytical data from a 10:1 *Z*/*E* mixture of **16**: IR (neat) 1734 cm^{-1}; ^1H NMR (*Z*) δ 7.69 (d, J=7.6 Hz, 1H), 7.61 (s, 1H), 7.39 (t, J=7.7 Hz, 1H), 7.27 (d, J=7.2 Hz, 1H), 7.15 (d, J=6.4 Hz, 1H), 5.49 (d, J=7.2 Hz, 1H), 5.11 (s, 1H), 4.99 (s, 1H), 3.86 (s, 3H), 2.20 (s, 3H); ^1H NMR (*E*, nonsuperimposed peaks) δ 7.74 (d, J=8.4 Hz, 1H), 1.88 (s, 3H); ^{13}C NMR (*Z*) δ 163.2 (+), 159.6 (+), 139.0 (+), 133.1 (−), 130.1 (+), 129.6 (−), 122.3 (−), 120.2 (−), 117.7 (+), 114.8 (−), 114.2 (−), 55.3 (−), 22.8 (−); GC–MS (EI) *m*/*z* 218 (M^+), 135 ($ArC{=}O^+$).

2-Methyl-3-butyn-2-yl benzoate (17).[21] and 3-methylbuta-1,3-dien-1-yl benzoate (18).[16,22] Reaction of **6** (700 mg, 2.00 mmol) in CH_2Cl_2 (30 mL) with benzoyl chloride (235 μL, 2.00 mmol) gave, after chromatography (hexanes–EtOAc, 19:1), a ca 4:1 mixture of **17** and **18** (99 mg, 0.25 mmol, 25%) followed by **17** (32 mg, 0.16 mmol, 8%). Analytical data for **17**: ^1H NMR δ 7.95 (dd, J=6.9 and 1.6, 2H), 7.48 (tt, J=7.3 and 1.2 Hz, 1H), 7.35 (dt, J=7.9 and 1.4 Hz, 2H), 2.51 (s, 1H), 1.75 (s, 6H); ^{13}C NMR δ 164.8 (+), 132.8 (−), 130.7 (+), 129.6 (−), 128.2 (−), 84.6 (+), 72.5 (+), 72.2 (+), 29.0 (−); Analytic data for **16** from 4:1 mixture of **17** and **18**: ^1H NMR

(*Z*/*E*>10:1, nonsuperimposed peaks) δ 8.02 (dd, *J*=7.1 and 1.4 Hz), 5.41 (d, *J*=7.3 Hz), 5.04 (s), 4.93 (s), 2.18 (s).

2-Methyl-3-butyn-2-yl 4-nitrobenzoate (19)[23] and 3-methylbuta-1,3-dienyl 4-nitrobenzoate (20). Reaction of **6** (699 mg, 2.00 mmol) in CH_2Cl_2 (30 mL) with 4-nitrobenzoyl chloride (378 mg, 2.00 mmol) as described above (24.5 h) gave, after chromatography (pentane–Et_2O, 19:1), **20** (11 mg, 0.05 mmol, 2%)[24] followed by **19** (43 mg, 0.18 mmol, 9%), both as white solids. Analytical data for **19**: mp 120–122°C; IR (neat) 3256, 1729, 1530 cm^{-1}; ^1H NMR δ 8.29 (d, *J*=8.7 Hz, 2H), 8.19 (d, *J*=8.9 Hz, 2H), 2.63 (s, 1H), 1.85 (s, 6H); ^{13}C NMR δ 162.9 (+), 150.5 (+), 136.2 (−), 130.7 (−), 125.5 (−), 83.9 (+), 73.6 (+), 73.2 (+), 28.9 (+); Anal. calcd for $C_{12}H_{11}NO_4$: C, 61.80; H, 4.75. Found: C, 61.63; H, 5.14. Analytical data for **20**: mp 103–106°C; IR (neat) 1737, 1526, 1266, 1102 cm^{-1}; ^1H NMR δ 8.35 (d, *J*=8.9 Hz, 2H), 8.27 (d, *J*=8.9 Hz, 2H), 7.26 (d, *J*=6.9 Hz, 1H), 5.56 (d, *J*=7.1 Hz, 1H), 5.14 (s, 1H), 5.06 (s, 1H), 2.18 (s, 3H); GC-MS (EI) *m*/*z* 233 (M^+), 150 (Ar–CO^+).

2-Methylbuta-1,3-dien-1-yl 4-methoxybenzoate (21). Reaction of **7**[25] (349 mg, 1.00 mmol) in CH_2Cl_2 (25 mL) with 4-methoxybenzoyl chloride (136 μL, 1.00 mmol) gave, after chromatography (pentane–Et_2O, 9:1), **21** (153 mg, 0.70 mmol, 70%). Analytic data from a 5.3:1 mixture of *Z*/*E*-**21**: mp 41–44°C; IR (neat) 1730 cm^{-1}; ^1H NMR (*Z* isomer) δ 8.07 (d, *J*=7.1 Hz, 2H), 7.50 (s, 1H), 6.95 (d, *J*=6.9 Hz, 2H), 6.43 (dd, *J*=17.2 and 10.7 Hz, 1H), 5.25 (d, *J*=17.2 Hz, 1H), 5.09 (d, *J*=10.9 Hz, 1H), 3.87 (s, 3H), 1.94 (d, *J*=1.2 Hz, 3H); ^1H NMR (*E* isomer, nonsuperimposed peaks) δ 7.27 (s, 1H), 7.07 (dd, *J*=17.6 and 10.9 Hz, 1H), 5.28 (d, *J*=17.6 Hz, 1H), 1.82 (d, *J*=1.4 Hz, 3H); ^{13}C NMR δ 163.8 (+), 162.8 (+), 136.1 (−), 135.6 (−), 132.4 (−), 131.9 (−), 131.0 (−), 121.3 (+), 120.8 (+), 118.6 (+), 114.4 (+), 113.8 (−), 112.6 (+), 55.4 (−), 13.9 (−), 9.7 (−).

2-Methylbuta-1,3-dien-1-yl 3-methoxybenzoate (22). Reaction of **7** (349 mg, 1.00 mmol) in CH_2Cl_2 (25 mL) with 3-methoxybenzoyl chloride (141 μL, 1.00 mmol) gave, after chromatography (hexanes–EtOAc, 9:1), **22** (163 mg, 0.74 mmol, 74%) as a colorless oil. Analytic data from a 3.8:1 mixture of *Z*/*E*-**22**. IR (neat) 1730, 1274, 1123 cm^{-1}; ^1H NMR (*Z* isomer) δ 7.72 (d, *J*=7.7 Hz, 1H), 7.61 (d, *J*=2.5 Hz, 1H), 7.51 (s, 1H), 7.39 (t, *J*=8.2 Hz, 1H), 7.15 (dd, *J*=8.4 and 2.2 Hz, 1H), 6.43 (dd, *J*=17.3 and 10.6 Hz, 1H), 5.27 (d, *J*=17.3 Hz, 1H), 5.12 (d, *J*=10.6 Hz, 1H), 3.87 (s, 3H), 1.95 (d, *J*=1.2 Hz, 3H); ^1H NMR (*E* isomer, nonsuperimposed peaks) δ 7.27 (s, 1H), 7.07 (dd, *J*=17.6 and 10.9 Hz, 1H), 5.29 (d, *J*=17.6 Hz, 1H), 1.83 (d, *J*=1.2 Hz, 3H); ^{13}C NMR δ 163.0 (+), 162.9 (+), 159.6 (+), 136.0 (−), 135.4 (−), 132.3 (−), 130.8 (−), 130.4 (+), 129.5 (−), 122.2 (−), 121.4 (+), 119.8 (−), 114.7 (+), 114.4 (−), 113.0 (+), 55.3 (−), 13.9 (−), 9.7 (−); GC–MS (EI) *m*/*z* 218 (M^+), 135 (ArC=O^+).

2-Methylbuta-1,3-dien-1-yl 4-nitrobenzoate (23). Reaction of **7** (349 mg, 1.00 mmol) in CH_2Cl_2 (25 mL) with 4-nitrobenzoyl chloride (190 mg, 1.00 mmol) gave, after chromatography (hexanes–EtOAc, 9:1), **23** (78 mg, 0.33 mmol, 33%) as a white solid. Analytic data from a 4:6:1 mixture of *Z*/*E*-**23**. Mp 82–85°C; IR (neat) 1736, 1526, 1272, 1138 cm^{-1}; ^1H NMR (*Z* isomer) δ 8.34 (d, *J*=9.2 Hz, 2H), 8.30 (d, *J*=9.1 Hz, 2H), 7.51 (s, 1H), 6.43 (dd, *J*=17.1 and 10.9 Hz, 1H), 5.33 (d, *J*=17.3 Hz, 1H), 5.18 (d, *J*=10.6 Hz, 1H), 1.97 (d, *J*=1.2 Hz, 3H); ^1H NMR (*E* isomer, nonsuperimposed peaks) δ 7.27 (s, 1H), 5.35 (d, *J*=17.3 Hz, 1H), 1.86 (d, *J*=1.5 Hz, 3H); ^{13}C NMR δ 161.3 (+), 161.2 (+), 150.8 (+), 135.5 (−), 134.9 (−), 134.5 (+), 131.9 (−), 130.9 (−), 130.4 (−), 123.7 (−), 122.5 (+), 120.4 (+), 115.7 (+), 114.0 (+), 13.9 (−), 9.7 (−); Anal. calcd for $C_{12}H_{11}NO_4$: C, 61.80; H, 4.75. Found: C, 61.90, 4.79.

2,4-Dimethoxybenzoic 3-methyl-2-butenoic anhydride (24). To a −40°C cold solution of **6** (350 mg, 1.00 mmol) in CH_2Cl_2 (30 mL) was added, under a positive flow of argon, 2,4-dimethoxybenzoyl chloride (201 mg, 1.00 mmol). The solution immediately turned deep red. After 1 h, the flask was opened to the air, and pyridine *N*-oxide (200 mg, 1.90 mmol) was added. The reaction mixture was allowed to slowly reach ambient temperature (25 h). The reaction mixture was filtered through Celite, and the Celite pad was washed with CH_2Cl_2 (20 mL). Removal of solvents from the filtrate followed by chromatography (pentane–Et_2O, 9:1 then pentane–Et_2O, 1:1) gave **24** (170 mg, 0.64 mmol, 64%) as a faint yellow solid. Mp 59–61°C; IR (neat) 1771, 1718, 1606, 1215, 1110, 1003 cm^{-1}; ^1H NMR δ 7.90 (d, *J*=8.7 Hz, 1H), 6.51 (dd, *J*=8.9 and 2.3 Hz, 1H), 6.46 (d, *J*=2.4 Hz, 1H), 5.83 (apparent t, *J*=1.3 Hz, 1H), 3.88 (s, 3H), 3.87 (s, 3H), 2.23 (s, 3H), 1.99 (s, 3H); ^{13}C NMR δ 165.7 (+), 162.4 (+), 162.3 (+), 161.7 (+), 135.2 (−), 115.3 (−), 110.7 (+), 105.3 (−), 98.8 (−), 56.0 (−), 55.7 (−), 27.8 (−), 20.8 (−); Anal. calcd for $C_{14}H_{16}O_5$: C, 63.63; H, 6.10. Found: C, 63.69; H, 6.24.

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