Thermal Decomposition of Pentacarbonyl(1-acyloxyalkylidene)chromium(0) Complexes: Formation of *Z*-Enol Esters

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Pentacarbonyl(1-acyloxyalkylidene)chromium(0) complexes, formed *in situ* by reaction of the corresponding tetramethylammonium pentacarbonyl(1-oxoalkyl)chromate(1−) salts with carboxylic acid halides, affords enol esters in moderate to good yields. In all cases examined, the *Z*-enol ester was obtained as the major or exclusive isomer. Addition of 1 equiv of pyridine to the reaction mixture substantially improved the *Z*/*E* ratio and, in most cases, increased the chemical yield.

Carbonyl(1-oxoalkyl)metalate 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, alkoxychromium carbenes are usually formed either 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 tetramethylammonium pentacarbonyl(1-oxoalkyl)chromate(1−) complexes with acyl halides followed by nucleophilic substitution of the formed acyloxy carbene, employing the appropriate alcohol. The intermediately 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.[3,4] Although this thermal instability is well known, few reports regarding the faith of these highly reactive acyloxy carbene complexes have been published.[5] We have communicated a novel elimination reaction utilizing pentacarbonyl(1-acyloxyalkylidene)chromium(0) complexes, formed *in situ* by reaction of tetramethylammonium pentacarbonyl(1-oxoalkyl)chromate(1−) salts and carboxylic acid halides, forming enol esters in good yields and with high *Z*/*E* ratios.[6,7] In our initial experiment, reaction of tetramethylammonium pentacarbonyl(acetyl)chromate(1−) (**1**) with benzoyl chloride at −40 °C followed by slow warming to ambient temperature, gave ethenyl benzoate (**2**) in 41% isolated yield (Scheme 1). In addition to the enol ester **2**, varying amounts of benzoic acid (**3**), and tetramethylammonium pentacarbonylchromium chloride, $NMe_4[(CO)_5CrCl]$ was formed.

Related elimination reactions forming enol ethers,[8] dihydrofuranes,[9] tetrahydropyrans,[10] imines,[11] ene carbamates,[12] vinylsilanes,[13] and alkenes[14] have been reported for alkoxy- and amino-substituted Fischer chromium carbenes under thermal conditions in the presence of a base. The *Z*-isomer is usually the predominant product obtained in these reactions.[15] We report herein a full account of the scope of the elimination reaction forming enol esters together with a brief study of the mechanism.

Results and Discussion

To evaluate the scope and limitations of the formation of enol esters, a number of tetramethylammonium pentacarbonyl(1-oxoalkyl)chromate(1−) complexes were reacted with carboxylic acid chlorides or bromides, and the results thereof are summarized in Table 1. Although varying amounts of the corresponding carboxylic acid

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(3) To our knowledge, pentacarbonyl[1-acyloxy(2-furyl)methylidene]-chromium(0) and pentacarbonyl[1-acyloxy(2-thienyl)methylidene]chromium(0) are the only acyloxy chromium complexes isolable at room temperature. (a) Connor, J. A.; Jones, E. M. *J. Chem. Soc. A* **1971**, 1974. (b) Fischer, E. O.; Selmayr, T.; Kreissl, F. R. *Chem. Ber.* **1977**, *110*, 2947. For an attempted intramolecular benzannulation of a related furyl complex, see: Wulff, W. D.; McCallum, J. S.; Kunng, F.-A. *J. Am. Chem. Soc.* **1988**, *110*, 7419.

(4) Thermally stable acyloxy complexes of iron and ruthenium have recently been reported; see: Adams, H.; Maloney, C. A.; Muir, J. E.; Walters, S. J.; Winter, M. J. *J. Chem. Soc., Chem. Commun.* **1995**, 1511.

(5) For a few reactions of acyloxy-substituted chromium carbenes, see: (a) Murray, C. K.; Yang, D. C.; Wulff, W. D. *J. Am. Chem. Soc.* **1990**, *112*, 5660. (b) Murray, C. K.; Warner, B. P.; Dragisich, V.; Wulff, W. D.; Rogers, R. D. *Organometallics* **1990**, *9*, 3142.

(6) Söderberg, B. C.; Turbeville, M. J. *Organometallics* **1991**, *10*, 3951.

(7) For a compilation of synthetic methods to prepare enol esters, see: Larock, R. C. *Comprehensive Organic Transformations*; VCH Publisher: New York, 1989; p 743. For some additional examples, see: (a) Doucet, H.; Martin-Vaca, B.; Bruneau, C.; Dixneuf, P. H. *J. Org. Chem.* **1995**, *60*, 7247. (b) Kowalski, C. J.; Haque, M. S. *J. Am. Chem. Soc.* **1986**, *108*, 1325. (c) Kikukawa, K.; Naritomi, M.; He, G.-X.; Wada, F.; Matsuda, T. *J. Org. Chem.* **1985**, *50*, 299. (d) Mitsudo, T.-a.; Hori, Y.; Watanabe, Y. *J. Org. Chem.* **1985**, *50*, 1567.

(8) (a) Barluenga, J.; Montserrat, J. M.; Florez, J.; Garcia-Granda, S.; Martin, E. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1392. (b) Harvey, D. F.; Neil, D. A. *Tetrahedron* **1993**, *49*, 2145. (c) Harvey, D. F.; Lund, K. P.; Neil, D. A. *J. Am. Chem. Soc.* **1992**, *114*, 8424. (d) Wulff, W. D.; Bauta, W. E.; Kaesler, R. W.; Lankford, P. J.; Miller, R. A.; Murray, C. K.; Yang, D. C. *J. Am. Chem. Soc.* **1990**, *112*, 3642. (e) Wulff, W. D.; Yang, D. C. *J. Am. Chem. Soc.* **1983**, *105*, 6726. (f) Casey, C. P.; Brunsvold, W. R. *Inorg. Chem.* **1977**, *16*, 391. (g) Fischer, E. O.; Maasböl, A. *J. Organomet. Chem.* **1968**, *12*, P15.

(9) (a) Schmidt, B.; Kocienski, P.; Reid, G. *Tetrahedron* **1996**, *52*, 1617. (b) Lattuada, L.; Licandro, E.; Maiorana, S.; Papagni, A. *J. Chem. Soc., Chem. Commun.* **1991**, 437. (c) Casey, C. P.; Anderson, *J. Chem. Soc., Chem. Commun.* **1975**, 895.

(10) (a) Barluenga, J.; Montserrat, J. M.; Florez, J.; Garcia-Granda, S.; Martin, E. *Chem. Eur. J.* **1995**, *1*, 236. (b) Aoki, S.; Fujimura, T.; Nakamura, E. *J. Am. Chem. Soc.* **1992**, *114*, 2985.

(11) Connor, J. A.; Rose, P. D. *J. Organomet. Chem.* **1972**, *46*, 329.

(12) Montgomery, J.; Wieber, G. M.; Hegedus, L. S. *J. Am. Chem. Soc.* **1990**, *112*, 6255.

(13) Iwasawa, N.; Saitou, M. *Chem. Lett.* **1994**, 231.

(14) Fischer, E. O.; Held, W. *J. Organomet. Chem.* **1976**, C59.

(15) For examples of *trans* selectivity, see: (a) McDonald, F. E.; Schultz, C. C.; Chatterjee, A. K. *Organometallics* **1995**, *14*, 3628. (b) Bernasconi, C. F.; Sun, W. *Organometallics* **1995**, *14*, 5615. (c) Aumann, R.; Läge, M.; Krebs, B. *Chem. Ber.* **1992**, *125*, 1627. (d) Fischer, E. O.; Plabst, D. *Chem. Ber.* **1974**, *107*, 3326.

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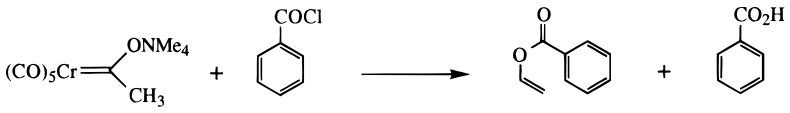
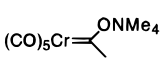
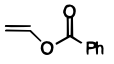
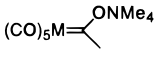
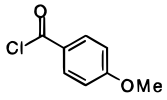
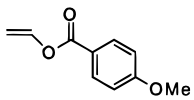
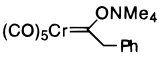
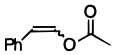
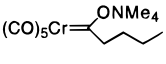
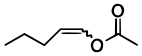
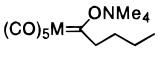
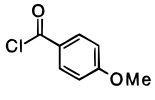
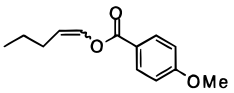
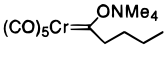
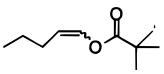
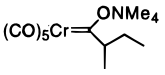
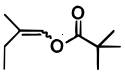
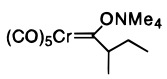
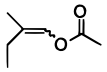
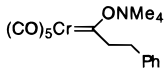
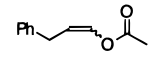
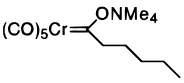
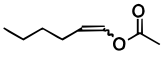
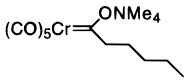
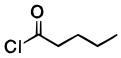
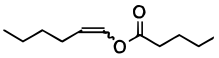
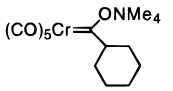
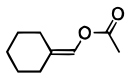
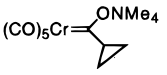
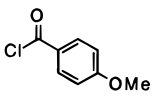
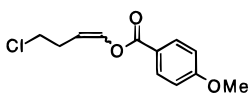
Scheme 1



1 **2** **3**

Table 1. Thermal Decomposition of *in Situ* Formed Pentacarbonyl(1-acyloxyalkyl)chromium(0) Complexes

Entry	Complex	Acid Halide	Product (Yield)[a]
			
1	**1**		**2** (41%)
2	**1**[b]		**2** (19%)
3	**1**[c]		**2** (73%)
			
4	**1-Cr**		**12** (<3%)
5	**1-Cr**[c]		**12** (73%)
6	**1-Mo**		**12** (<3%)
7	**1-Mo**[c]		**12** (73%)
8	**1-W**		**12** (<3%)
9	**1-W**[c]		**12** (93%)
			
10	**4**		**13** (70%, *Z*/*E* >20:1)
			
11	**5**		**14** (13%, *Z*/*E* >20:1)
			
12	**5-Cr**		**15** (74%, *Z*/*E* = 15:1)
13	**5-Cr**[d]		**15** (17%, *Z*/*E* >20:1)
14	**5-W**		**15** (<3%)
15	**5-W**[c]		**15** (14%, *Z*/*E* >20:1)
			
16	**5**		**16** (49%, *Z*/*E* = 6:1)
17	**5**[b]		**16** (55%, *Z*/*E* = 7.6:1)
18	**5**[c]		**16** (40%, *Z*/*E* = 10:1)
			
19	**6**		**17** (46%, *Z*/*E* = 1.5:1)
			
20	**6**		**18** (21%, *Z*/*E* = 1.7:1)
			
21	**7**		**19** (26%, *Z*/*E* = 17:1)
22	**7**[c]		**19** (40%, *Z*/*E* = 40:1)
			
23	**8**		**20** (31%, *Z*/*E* = 19:1)
			
24	**8**		**21** (54%, *Z*/*E* = 13:1)
25	**8**[c]		**21** (82%, *Z*/*E* >20:1)
			
26	**9**		**22** (65%)
			
27	**10**		**23** (39%, *Z*/*E* >15:1)
28	**10**		**24** (<3%)
29	**10**[c]		**24** (24%, *Z*/*E* >20:1)
30	**11**		**12** (5%)

[a] Isolated yield after chromatography or short-path distillation. A ratio of >20:1 and >15:1 was assigned for reactions where only one isomer was detected by ^{1}H NMR or GLC. For reactions where a minute amount of product was visible by enlargement of the crude ^{1}H NMR spectra, a yield of <3% was assigned. [b] Reaction performed at ambient temperature. [c] 1 equiv of pyridine was added. [d] Formed *in situ* from reaction of the corresponding lithium salt with 1.1 equiv of tetramethylammonium chloride.

were observed by ^{1}H NMR of the crude reaction mixtures, only the enol esters were isolated and characterized. The origin of the acid byproduct in these reactions is ambiguous and will be discussed below.

As seen in Table 1, enol esters are formed using both acid chlorides and acid bromides (entries 10 and 11). The size of the acid halide has a substantial effect on the stereoselectivity of the reaction. For a given carbene complex, increasing the size of the ester moiety decreased the *Z*/*E* ratio. This effect is clearly illustrated employing complex **5** where the *Z*/*E* ratio of the isolated enol esters decreased from >20:1 to 15:1 to 6:1 using acetyl bromide, 4-methoxybenzoyl chloride, and 2,2-dimethylpropanoyl chloride, respectively (entries 11, 12, and 16). The same general trend was observed upon reaction of complex **6** with acetyl chloride and 2,2-dimethylpropanoyl chloride and upon reaction of complex **8** with acetyl chloride and pentanoyl chloride (entries 19, 20 and 23, 24, respectively). In the former two cases, trisubstituted enol esters were obtained.

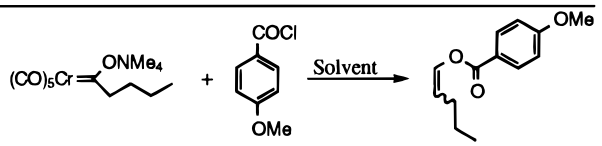
The importance of the counterion was clearly demonstrated by employing lithium or magnesium iodide pentacarbonyl(1-oxopentyl)chromate(1−) salts in place of the tetramethylammonium complex **5**. Thus, reaction of lithium pentacarbonyl(1-oxopentyl)chromate(1−), formed *in situ* by the addition of *n*-butyllithium to a slurry of chromium hexacarbonyl in diethyl ether with 4-methoxybenzoyl chloride, gave a complex mixture of unidentified products together with a small amount of **15** (<3%).[16] A similar result was obtained when *n*-butylmagnesium iodide was used in place of *n*-butyllithium. Formation of complex **5**, *in situ*, by reaction of a dichloromethane solution of the lithium salt with 4-methoxybenzoyl chloride, in the presence of 1.1 equiv of tetramethylammonium chloride, gave a 17% yield of **15** (entry 13).[17]

The outcome of the reaction of complex **1** changed dramatically employing 4-methoxybenzoyl chloride in place of benzoyl chloride (entry 4). In fact, all group 6 pentacarbonyl(1-oxoalkyl)metalate(1−) salts gave a very minute amount of the expected enol ester (entries 4, 6, and 8). In sharp contrast, addition of 1 equiv of pyridine to the reaction mixture gave good to excellent yields of **12** starting from **1-Cr** (73%), **1-Mo** (73%), and **1-W** (93%), respectively (entries 5, 7, and 9). It should be noted that addition of pyridine also gave a substantially higher yield of **2** (entry 3). 4-Methoxybenzoyl chloride forms enol esters with other complexes and is therefore not, as such, detrimental to the reaction. For example, a good yield of enol ester **15** was obtained upon reaction of complex **5** with 4-methoxybenzoyl chloride (entry 12). A modest yield of **15** was obtained using **5-W** but only in the presence of pyridine (entry 15).

In a comparison study evaluating the influence of solvent on the yield and the *Z*/*E* ratio, complex **5** was reacted with 4-methoxybenzoyl chloride at ambient temperature. As can be seen in Table 2, our initial choice of solvent, dichloromethane, proved superior to any other solvents investigated, with regard to both chemical yield and isomer ratio. We do not have an explanation for this solvent effect.

Some substrates appear to be sensitive to the initial reaction temperature: for example, a substantially lower yield of **2** was obtained when the reaction vessel was removed from the cold bath immediately after the addition of benzoyl chloride to **1** (entry 2). Other complexes were not negatively affected by higher reaction temperatures, *e.g.*, both **15** and **16** were obtained in a higher or comparable yield upon addition of the acid chloride at room temperature (Table 1, entry 17; Table 2, entry 1). It was usually noted that a somewhat cleaner crude product was obtained using the original reaction conditions.

Table 2. Influence of Solvent on Yield and Isomer Ratio



Solvent[a]	*Z*/*E*[b]	Yield[c]
Dichloromethane	15.6 : 1	73%
Pentane[d]	6.3 : 1	56%
Benzene[d]	6.4 : 1	45%
Tetrahydrofurane	3.9 : 1	57%
Acetonitrile	4.7 : 1	40%
Acetone	4.2 : 1	40%
Ethyl acetate	4.4 : 1	52%

[a] 1 mmol of **5** and 1.1 mmol of 4-methoxybenzoyl chloride in 15 mL of solvent at room temperature. [b] By ^{1}H NMR integration. [c] Isolated yield after air oxidation and column chromatography. [d] The complex is insoluble or only partially soluble in this solvent.

The present methodology compares favorably, in some cases, to a ruthenium-catalyzed reaction recently published by Dixneuf *et al.*[18] Although *Z*-enol esters were generally produced in high yields, some examples of relatively unsatisfactory results were reported. For example, enol esters **20** (35%, *Z*/*E* = 10:1) and **21** (35%; *Z*/*E* = 49:1) were both prepared in low yield by the ruthenium-catalyzed addition of carboxylic acids to terminal alkynes. In comparison, the carbene-based methodology gave a similar yield of **20** having a much higher *Z*/*E* ratio and afforded a substantially higher yield of **21**, especially in the presence of pyridine (entries 23−25). Since only one isomer of **21** was isolated in both cases, a comparison of the *Z*/*E* ratios could not be made. Our protocol also allows for the formation of trisubstituted enol esters, not available by the ruthenium-catalyzed methodology.

In addition to the acyclic complexes discussed above, some cyclic substrates were also examined. Treatment of complex **9** with acetyl chloride produced the expected product **22** in good yield (entry 26). Reaction of the cyclopropyl-substituted complex **10** with 4-methoxybenzoyl chloride gave, in place of an exocyclic enol ester, the chloro-substituted *Z*-enol ester **23** in 39% isolated yield (entry 27).[19] A related product was formed by reaction of **10** with acetyl chloride in the presence of pyridine (entry 29). The latter product was not observed in the absence of base (entry 28), corroborating an experiment previously reported by Connor and Jones.[20] Nucleophilic

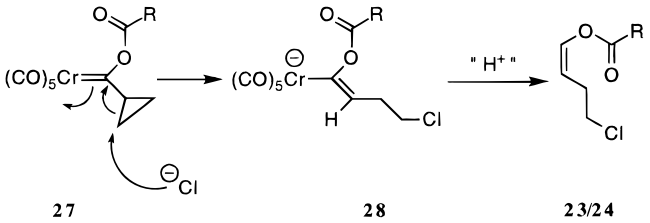
(16) A small amount of product was seen upon expansion of the alkene region of the crude ^{1}H NMR spectra.

(17) For a recent example of O-alkylation of Fischer carbene complexes using tetraalkylammonium salts, see: Hoye, T. R.; Chen, K.; Vyvyan, J. R. *Organometallics* **1993**, *12*, 2806.

(18) Doucet, H.; Martin-Vaca, B.; Bruneau, C.; Dixneuf, P. H. *J. Org. Chem.* **1995**, *60*, 7247.

(19) For a related ring opening, see: Primke, H.; Sarin, G. S.; Kohlstruk, S.; Adiwidjaja, G.; de Meijere, A. *Chem. Ber.* **1994**, *127*, 1051.

Scheme 2



27 **28** **23/24**

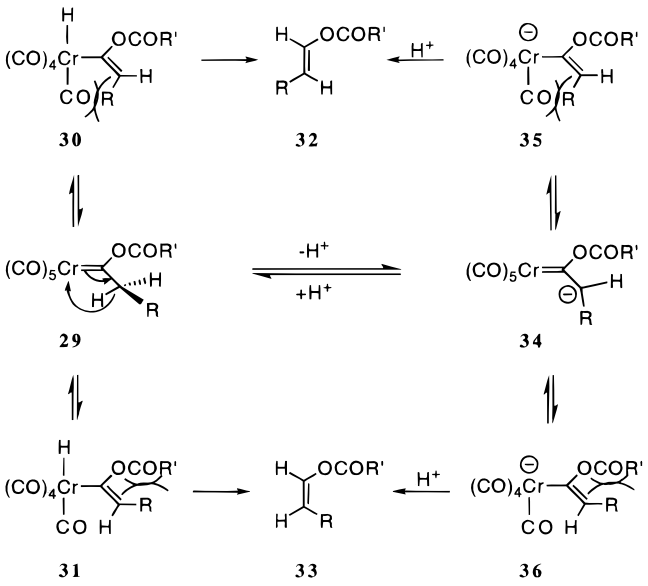
cleavage of the intermediately formed acyloxy complex **27**, producing the anion **28** followed by protonation, is a plausible mechanism for the formation of **23** and **24** (Scheme 2).[21,22] It is interesting to note that reaction of **10** with 4-methoxybenzoyl chloride in the presence of D_2O gave no identifiable products.

As a final example, reaction of the trimethylsilyl-substituted carbene **11** with 4-methoxybenzoyl chloride gave the enol ester **12** in a very low yield (5%, entry 30). Products derived from a thermally induced 1,2-migration of the silyl group were not observed as previously reported in some similar systems.[23] In a closely related study by Connor and Jones, the enol ester product was not observed upon reaction of the 2-(trimethylsilyl)alkyl complex **11** with acetyl chloride. The investigators isolated tetramethylammonium pentacarbonylchromium-(II) chloride, $NMe_4[(CO)_5CrCl]$, as the sole product in quantitative yield.[24] Although not identified, it is plausible that an organic product similar to that reported herein was formed but lost during workup.

The stereochemistry of the enol esters was deduced from their ^{1}H NMR spectra. Relatively small H−H coupling constants, $J = 6.3-8.0$ Hz, were observed across the double bond typical for a *Z*-configuration; whereas the same coupling constants for the minor *E*-enol esters were 12.3−12.6 Hz. The stereochemistry of the trisubstituted esters **17** and **18** was assigned by comparison with literature chemical shift values (for **18**) and by comparison between the two compounds. The C*H*-OAc proton of **18** resonates for the *E*-isomer at δ 6.72 and for the *Z*-isomer at δ 6.87. A similar upfield shift (0.08 ppm) fo the *E*-isomer was observed for **17**.[25]

A number of possible mechanistic rationales can be proposed for the formation of the enol esters (Scheme 3). Acylation of a tetramethylammonium pentacarbonyl(1-oxoalkyl)chromate(1−) salt affords an unstable acyloxy carbene (**29**). β-Hydrogen elimination would give either of the σ-alkylchromium hydride species **30** or **31**. Two main steric interactions are to be expected in complexes of this structure: either interactions between the alkyl group in **30** and chromium-bound hydride or a carbon monoxide ligand (shown for carbon monoxide in Scheme 3) or interactions between the alkyl group and the ester moiety in **31**. In all cases, the carbon monoxide ligand and the hydride are more sterically demanding in comparison to the ester group; thus, β-elimination to the less sterically congested intermediate **31** is preferred. Reductive elimination from **30** or **31** producing the product **32** or **33**, respectively, completes the sequence of events.[26] Increasing the size of the ester group should, according to this mechanism, decrease the *Z*/*E* ratio which has been experimentally confirmed (see above discussion). Another mechanistic possibility that can be entertained is an acid−base equilibrium between **29** and **34**−**36**. Protonation of the anions on either carbon or chromium would again give the observed products. Protonation of anionic molybdenum carbenes using Et_3NH^+ and chromium carbenes using HCl has been shown to give *Z*-enol ethers.[27,28] The same steric arguments invoked for **30** and **31** can be used for **35** and **36**. The presence of a base, such as pyridine, would shift the equilibrium toward the intermediates **34**−**36**, possibly explaining why a base is beneficial for the reaction. The role of pyridine in the case of complex **10** is unclear. Pyridine is not needed for deprotonation of the starting material but still has a remarkable influence on the yield of the reaction (entries 28−29).

Scheme 3



30 **32** **35** **29** **34** **31** **33** **36**

The following reaction sequence was performed to lend some support to the proposed mechanism for the β-elimination pathway. Reduction of methyl phenylethanoate with lithium aluminum deuteride gave the dideuterated alcohol **37** (Scheme 4). The alcohol was transformed using iodine, triphenylphosphine, and imidazole into the iodide **38** which was treated in sequence with *tert*-butyllithium, chromium hexacarbonyl, and tetramethylammonium bromide to produce complex **39** in good overall yield. Reaction of this complex with acetyl chloride gave the *cis*-enol ester **40** (*Z*/*E* = 11:1). The structure and stereochemistry of **40** were deduced from its ^{1}H and ^{13}C NMR spectra. In the ^{1}H NMR spectra,

(20) Connor, J. A.; Jones, E. M. *J. Chem. Soc., Dalton Trans.* **1973**, 2119

(21) A similar mechanism for the cleavage of pentacarbonyl[1-(thiophenyl)-1-cyclopropylmethylidene]chromate(0) complexes forming related thioenol ethers has been proposed. Herndon, J. W.; Reid, M. D. *J. Am. Chem. Soc.* **1994**, *116*, 383.

(22) For a related cleavage of cyclopropyl-substituted molybdenum carbynes using carboxylic acid halides, see: Carter, J. D.; Schoch, T. K.; McElwee-White, L. *Organometallics* **1992**, *11*, 3571.

(23) (a) Herndon, J. W.; Patel, P. P. *J. Org. Chem.* **1996**, *61*, 4500. (b) Macomber, D. W.; Madhukar, P. *Organometallics* **1991**, *10*, 2121.

(24) Connor, J. A.; Jones, E. M. *J. Organomet. Chem.* **1973**, *60*, 77.

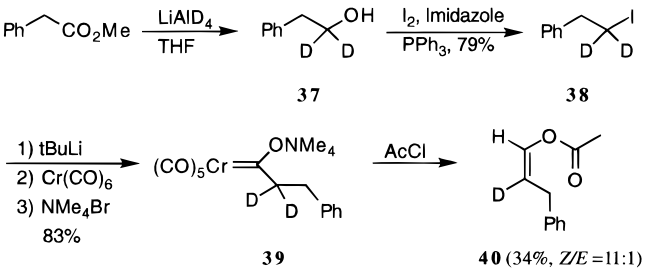
(25) For similar shifts of related compounds, see: (a) Wasserman, H. H.; Keller, L. S. *Tetrahedron Lett.* **1974**, *15*, 4355. (b) House, H. O.; Kramer, V. *J. Org. Chem.* **1963**, *28*, 3362.

(26) Related thermal 1,3-hydrogen shift−reductive elimination has previously been observed upon metathesis of molybdenum carbene complexes. (a) Harvey, D. F.; Neil, D. A. *Tetrahedron* **1993**, *49*, 2145. (b) Harvey, D. F.; Brown, M. F. *J. Org. Chem.* **1992**, *57*, 5559. See also: Katz, T. J.; Yang, G. X.-Q. *Tetrahedron Lett.* **1991**, *42*, 5895.

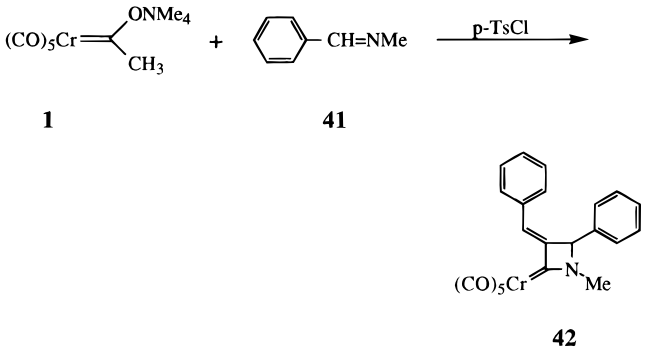
(27) (a) McDonald, F. E.; Schultz, C. C. *J. Am. Chem. Soc.* **1994**, *116*, 9363 and references therein. (b) McDonald, F. E.; Connoly, C. R.; Gleason, M. M.; Towne, T. B.; Treiber, K. D. *J. Org. Chem.* **1993**, *58*, 6952.

(28) Casey, C. P.; Brunsvold, W. R. *J. Organomet. Chem.* **1974**, *77*, 345.

Scheme 4



Scheme 5



the PhCH_2 resonance appeared as a doublet in **19** and as a broadened singlet in **40**, slightly shifted downfield relative to **19**. As was observed earlier, the CH_2 of the *Z*-isomer was shifted downfield by 0.09 ppm relative to the same signal for the *E*-isomer. Only one triplet resonance at δ 112.2 was observed in the ^{13}C NMR spectra belonging to C=*C*D−CH_2−R; thus, only one deuterium remained after the reaction. The corresponding resonance for the undeuterated product **19** is found at δ 112.4. With this result in hand, we were not surprised to isolate **40** as a single stereoisomer (33%, *Z*/*E* > 35:1) from a similar reaction of **39** with acetyl chloride in the presence of pyridine. It should be noted that the yield from the reactions of **7** and **39** with acetyl chloride is similar, indicating the absence of an isotope effect for this reaction. Based on the outcome of the reactions using deuterated starting material, the proposed β-hydride elimination−reductive elimination mechanism appears not be in operation in either the presence or absence of base. The source of the proton added to the carbon bearing the acetate is unknown. In an additional experiment, a solution of complex **1** in CD_2Cl_2 was treated with 4-methoxybenzoyl chloride in the presence of pyridine. Although **12** was isolated in 73% yield, no incorporation of deuterium was observed.

Finally, the origin of benzoic acid, shown in Scheme 1, is uncertain; it may have been formed during workup by hydrolysis of unreacted benzoyl chloride and/or hydrolysis of vinyl benzoate. A third possibility is direct elimination of benzoic acid from the intermediate benzyloxy complex to give the highly reactive pentacarbonyl(ethenylidene)-chromium complex, $(CO)_5Cr{=}C{=}CH_2$. A related elimination reaction wherein **1** was reacted with *p*-toluenesulfonyl chloride in the presence of the imine **41** to give complex **42** (25%, Scheme 5) has been reported by Barett *et al.*[29,30] Elimination of *p*-toluenesulfonic acid at some point in the reaction was proposed.

(29) (a) Barett, A. G. M.; Brock, C. P.; Sturgess, M. A. *Organometallics* **1985**, *4*, 1903. (b) Barett, A. G. M.; Mortier, J.; Sabat, M.; Sturgess, M. A. *Organometallics* **1988**, *7*, 2553.

(30) For a related formal elimination of water, see: Weiss, K.; Fischer, E. O.; Müller, J. *Chem. Ber.* **1974**, *107*, 3548.

In conclusion, a novel reaction of *in situ* formed pentacarbonyl(1-acyloxyalkylidene)chromium(0) complexes affording enol esters has been developed. Depending on substrate, moderate to good chemical yields of enol esters have been realized with a high *Z*/*E* selectivity. The presence of pyridine usually results in both a yield increase and a selectivity increase. Reactions of related unsaturated pentacarbonyl(1-acyloxyalkenylidene)chromium(0) complexes with acid halides are presently being pursued in our laboratories.

Experimental Section

General Procedures. Chemicals prepared according to literature procedures have been footnoted the first time used; all chemicals used herein were prepared as described below or obtained from commercial sources and used as received. Tetrahydrofuran (from sodium benzophenone ketyl) and CH_2Cl_2 (from CaH) were distilled prior to use. All reactions were performed in one-necked flasks having an attached side arm for the introduction of the inert atmosphere. All glassware was dried in an oven, at 140 °C, before use. Solvents were removed from all reaction mixtures and products on a rotary evaporator at water aspirator pressure. For the enol acetates, a 0−5 °C cold bath was used to minimize product evaporation during solvent removal. Silica gel (200−400 mesh) was used for chromatography.

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 (0.00, ^{1}H and ^{13}C), $CDCl_3$ (77.00, ^{13}C), or DMSO-d_6 (39.60, ^{13}C) internal standards. Multiplicities observed in off-resonance-decoupled ^{13}C NMR experiments are shown in parentheses. ^{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 $CDCl_3$, (−) denotes CH_3 or CH and (+) denotes CH_2 or C.

Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN, or Atlantic Microlab, Inc., Norcross, GA. We were unable to obtain a consistent elemental analysis for 2-methyl-1-buten-1-yl 2,2-dimethylpropanoate due to rapid hydrolysis even at −18 °C.

Tetramethylammonium Pentacarbonyl(1-oxohexyl)-chromate(1−) (8). To a −78 °C cold solution of 2-bromopentane (3.1 mL, 25.0 mmol) in Et_2O (50 mL) was added *tert*-butyllithium (31.0 mL, 52.7 mmol, 1.7 M in hexanes) *via* cannula over a 3 min period. The solution was stirred for 1 h, producing a yellow solution which was transferred *via* cannula to a 0 °C cold slurry of $Cr(CO)_6$ (5.50 g, 25.0 mmol) in Et_2O (100 mL). After stirring for 1 h at 0 °C and 1 h at ambient temperature, the solvents were removed from the formed brown reaction mixture. The resulting brown solid residue was stirred vigorously with a solution of tetramethylammonium bromide (7.70 g, 50.0 mmol) in degassed water (100 mL) for 20 min. The resulting yellow slurry was extracted with CH_2Cl_2 (3 × 75 mL), dried ($MgSO_4$), filtered (Celite), and evaporated to dryness affording **8** (4.1 g, 11.2 mmol, 45%) as pale yellow crystals: mp 92−94 °C dec; ^{1}H NMR (DMSO-d_6, br peaks) δ 3.4 (2 H), 3.2 (12 H), 2.6 (2 H), 1.2 (4 H), 0.9 (3 H); ^{13}C NMR (DMSO-d_6) δ 287.3 (+), 228.4 (+, *trans*-CO), 224.1 (+, *cis*-CO), 65.7 (+), 54.8 (−), 31.3 (+), 23.3 (+), 22.3 (+), 14.0 (−); IR (CH_2Cl_2) 2028, 1896 cm^{-1}.

Tetramethylammonium Pentacarbonyl(cyclohexyl-carbonyl)chromate(1−) (9). A flask, charged with a stir bar and graphite (2.34 g, 195 mmol), was heated (150−160 °C) on a sand bath for 10 min. Under a positive flow of argon, small pieces of potassium (0.95 g, 24.3 mmol) were added followed by heating (160 °C, 1 h). The flask was cooled to −78 °C, and THF (35 mL) and chromium hexacarbonyl (2.42 g, 11.0 mmol) were added to the bronze-colored laminate under positive flow of argon (PYROPHORIC!). The resulting slurry was stirred (−78 °C, 30 min; 0 °C, 30 min) followed by cooling (−78 °C)

and addition of cyclohexane carbonyl chloride (1.34 mL, 10.0 mmol) *via* syringe. After stirring (−78 °C, 30 min; 0 °C, 30 min), the solvents were removed. The resulting residue was stirred vigorously (20 min) with a solution of tetramethylammonium bromide (3.08 g, 20.0 mmol) in degassed water (50 mL). CH_2Cl_2 (40 mL) was added; the phases were separated, and the aqueous phase was extracted with CH_2Cl_2 (3 × 40 mL). The combined organic phases were dried ($MgSO_4$), filtered (Celite), and evaporated to dryness affording **9** (2.50 g, 6.60 mmol, 66%) as pale yellow crystals.[31]

Tetramethylammonium Pentacarbonyl(2,2-*d*,*d*-1-oxo-3-phenylpropyl)chromate(1−) (39). A 100 mL flask equipped with a stir bar was flame-dried and filled with argon. 1,1-Dideuterio-2-phenyl-1-iodoethane (**38**) (1.25 g, 5.34 mmol) and Et_2O (50 mL) were added to the flask. The solution was cooled to −20 °C; *tert*-butyllithium (10.20 mmol, 6 mL, 1.7 M in pentane) was added to the flask, and the resulting pale yellow solution was stirred at −20 °C (0.5 h) and then at ambient temperature (1 h). The solution was transferred *via* cannula to an airless flask containing a slurry of $Cr(CO)_6$ (1.10 g, 5.00 mmol) in Et_2O (20 mL). The resulting brown solution was stirred at ambient temperature (1 h) followed by solvent removal at reduced pressure. The brown residue was dissolved in degassed water (60 mL), and Me_4NBr (3.08 g, 20.00 mmol) was added in one portion under vigorous stirring. The resulting aqueous phase containing a yellow oil was extracted with CH_2Cl_2 (3 × 50 mL); the combined organic phases were dried ($MgSO_4$) and filtered, and the solvents were removed to give **39** (1.67 g, 4.16 mmol, 83 %) as a yellow solid. The complex rapidly decomposes at ambient temperature and was used immediately after isolation:[32] mp 42−44 °C dec; IR (CH_2Cl_2) 2029, 1887 cm^{-1}; ^{13}C NMR (67.5 MHz)[33] δ 284.7 (+), 228.0 (+), 223.8 (*cis*-CO, +), 142.9 (+), 128.1 (−), 128.1 (−), 125.1 (−), 55.2 (br, −), 29.7 (+).

Ethenyl Benzoate (2). To a −40 °C cold slurry of tetramethylammonium pentacarbonyl(acetyl)chromate(1−) (**1**)[34] (309 mg, 1.00 mmol) in CH_2Cl_2 (10 mL) was added benzoyl chloride (116 μL, 1.00 mmol) *via* syringe. The color immediately changed from yellow-green to red-brown. The reaction mixture was kept in a freezer at −20 °C (19 h) followed by ambient temperature (6 h), whereupon the solution slowly turned orange-yellow and an orange-yellow precipitate appeared. The solvent was removed on a rotary evaporator at water aspirator pressure to give a solid residue. The residue was triturated with pentane (40 mL) and filtered, leaving a yellow solid ($NMe_4Cr(CO)_5Cl$),[20,35] followed by solvent removal from the filtrate giving 241 mg of a yellow-white solid residue. ^1H NMR of the residue showed resonances assigned to vinyl benzoate and benzoic acid. The crude product was dissolved in Et_2O (30 mL), washed with $NaHCO_3$ (aq, 10%, 3 × 20 mL), dried ($MgSO_4$), filtered, and evaporated *in vacuo* to give **2** (60 mg, 0.41 mmol, 41%) as a faint yellow oil. Spectral data were in complete accordance with a commercially available sample (Aldrich).

A solution of **1** (309 mg, 1.00 mmol) and pyridine (81 μL, 1.00 mmol) in CH_2Cl_2 (20 mL) was reacted, at −40 °C, with benzoyl chloride (116 μL, 1.00 mmol) as described above. The reaction mixture was allowed to reach ambient temperature slowly (20 h). The formed yellow suspension was filtered (Celite), and the solvent was removed to give an orange semisolid residue. The crude product was purified by chromatography (pentane−Et_2O, 9:1) affording **2** (110 mg, 0.74 mmol, 74%) as a colorless oil followed by $(CO)_5CrC_5H_5N$ (172 mg, 0.63 mmol, 63%) as bright yellow crystals.[36]

Ethenyl 4-Methoxybenzoate (12). A solution of tetramethylammonium pentacarbonyl(acetyl)chromate(1−) (**1**) (309 mg, 1.00 mmol) and pyridine (81 μL, 1.00 mmol) in CH_2Cl_2 (20 mL) was reacted at −40 °C, with 4-methoxybenzoyl chloride (141 μL, 1.04 mmol) as described above. The reaction mixture was allowed to reach ambient temperature slowly (20 h). The formed yellow suspension was filtered (Celite), and the solvent was removed to give an orange semisolid residue. The crude product was purified by chromatography (pentane−Et_2O, 9:1) affording **12** (130 mg, 0.73 mmol, 73%) as white crystals[37] followed by $(CO)_5CrC_5H_5N$.

Tetramethylammonium pentacarbonyl(acetyl)tungstate(1−) (**1-W**)[34] (441 mg, 1.00 mmol) and pyridine (81 μL, 1.00 mmol) in CH_2Cl_2 (10 mL) were reacted at −40 °C with 4-methoxybenzoyl chloride (141 μL, 1.04 mmol), as described above. The reaction mixture was allowed to reach ambient temperature slowly (24 h). The formed yellow suspension was filtered (Celite), and the solvent was removed to give an orange semisolid residue. The crude product was purified by chromatography (pentane−Et_2O, 9:1) affording **12** (165 mg, 0.93 mmol, 93%) as white crystals followed by $(CO)_5WC_5H_5N$ (126 mg, 0.31 mmol, 31%) as yellow crystals.[36]

Tetramethylammonium pentacarbonyl(acetyl)molybdate(1−) (**1-Mo**)[34] (353 mg, 1.00 mmol) and pyridine (81 μL, 1.00 mmol) in CH_2Cl_2 (10 mL) were reacted at −40 °C with 4-methoxybenzoyl chloride (141 μL, 1.04 mmol), as described above. The reaction mixture was allowed to reach ambient temperature slowly (24 h). The formed yellow suspension was filtered (Celite), and the solvent was removed to give an orange semisolid residue. The crude product was purified by chromatography (pentane−Et_2O, 9:1) affording **12** (130 mg, 0.73 mmol, 73%) as white crystals followed by $(CO)_5MoC_5H_5N$ (100 mg, 0.32 mmol, 32%) as yellow crystals.[36]

(*Z*)-2-Phenyl-1-ethenyl Acetate (13). Acetyl chloride (142 μL, 2.00 mmol) was added dropwise by syringe to a −40 °C cold slurry of tetramethylammonium pentacarbonyl(1-oxo-2-phenylethyl)chromate(1−) (**4**)[38] (770 mg, 2.00 mmol)[39] in CH_2Cl_2 (30 mL). The reaction mixture was allowed to slowly reach ambient temperature. After 20 h, the formed faint yellow solution containing a yellow precipitate was filtered (Celite), and the filter was washed with pentane (10 mL). The solvents were removed on a rotary evaporator at water aspirator pressure to give a pale green oil containing $Cr(CO)_6$. The crude oil was purified by chromatography (hexanes) to give **13** (227 mg, 1.40 mmol, 70%) as a colorless oil after solvent removal.[18,40] Only the *Z*-isomer was observed by ^1H NMR (300 MHz).

(*Z*)-1-Penten-1-yl Acetate (14). Reaction of tetramethylammonium pentacarbonyl(1-oxopentyl)chromate(1−) (**5**)[41] (1.41 g, 4.00 mmol) with acetyl bromide (296 μL, 4.00 mmol) in CH_2Cl_2 (60 mL) at −40 °C to ambient temperature (20 h), as described above, gave, after solvent removal at water aspirator pressure (0 °C) and chromatography (pentane followed by pentane−Et_2O, 8:2), **14** (69 mg, 0.53 mmol, 13%, *Z*/*E* > 20:1) as a faint yellow oil.[42] The crude ^1H NMR showed some additional products that could not be isolated and identified.

(*Z*)-1-Penten-1-yl 4-Methoxybenzoate (15). Reaction of tetramethylammonium pentacarbonyl(1-oxopentyl)chromate(1−) (**5-Cr**) (351 mg, 1.00 mmol) with 4-methoxybenzoyl chloride (136 μL, 0.97 mmol) in CH_2Cl_2 (10 mL) at −40 °C, as described above, gave, after evaporation and short column chromatography (ethanol), **15** (158 mg, 0.72 mmol, 74%, *Z*/*E* = 15:1) as a colorless oil. *Z*-**15**: IR (film) 2950, 1720, 1595, 1250, 1160, 1090, 1020 cm^{-1}; ^1H NMR (90 MHz) δ 8.06 (d, J = 9.1 Hz, 2 H), 7.25 (td, J = 6.4, 1.5 Hz, 1 H), 6.95 (d, J = 9.1

(31) This compound has previously been prepared *via* a different route; see: Murray, C. K.; Yang, D. C.; Wulff, W. D. *J. Am. Chem. Soc.* **1990**, *112*, 5660.

(32) An interpretable ^1H NMR spectrum could not be obtained; only broad unresolved signals were observed.

(33) The resonance for the carbon bearing the deuterium atoms was not found.

(34) Fischer, E. O.; Maasböl, A. *Chem. Ber.* **1967**, *100*, 2445.

(35) Abel, E. W.; Butler, I. S.; Reid, J. G. *J. Chem. Soc.* **1963**, 2068.

(36) Hor, T. S. A. *Inorg. Chim. Acta* **1988**, *143*, 3.

(37) (a) Rekasheva, A. F.; Kulish, L. F.; Kiprianova, L. A. *Theor. Exp. Chem.* **1971**, *7*, 218. (b) Rao, Y. S.; Filler, R. *J. Org. Chem.* **1971**, *36*, 1447.

(38) Söderberg, B. C.; Hegedus, L. S.; Sierra, M. A. *J. Am. Chem. Soc.* **1990**, *112*, 4364.

(39) The complex is not completely soluble in CH_2Cl_2 at −40 °C.

(40) Yamane, T.; Kikukawa, K.; Takagi, M.; Matsuda, T. *Tetrahedron Lett.* **1973**, 955.

(41) Thompson, D. K.; Suzuki, N.; Hegedus, L. S.; Satoh, Y. *J. Org. Chem.* **1992**, *57*, 1461.

(42) Cousineau, T. J.; Cook, S. L.; Seacrist, J. A., III *Synth. Commun.* **1979**, *9*, 157.

Hz, 2 H), 4.98 (td, J = 7.6, 6.4 Hz, 1 H), 3.87 (s, 3 H), 2.26 (q, J = 6.6 Hz, 2 H), 1.47 (sextet, J = 6.9 Hz, 2 H), 0.96 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (22.5 MHz) δ 163.7, 163.4, 134.4, 132.0 (2C), 121.8, 114.1, 113.8 (2C), 55.5, 26.7, 22.4, 13.7; MS (EI) m/z 220 (M^+). Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.88; H, 7.32. Found: C, 71.22; H, 7.61.[43]

A solution of tetramethylammonium pentacarbonyl(1-oxopentyl)tungstate(1−)[44] (**5-W**) (483 mg, 1.00 mmol) and pyridine (81 μL, 1.00 mmol) in CH_2Cl_2 (10 mL) was reacted, at −40 °C, with 4-methoxybenzoyl chloride (141 μL, 1.04 mmol) as described above, affording **15** (32 mg, 0.14 mmol, 14%) as a colorless oil.

n-Butyllithium (1.6 M in hexanes, 1.88 mL, 3.00 mmol) was added to a slurry of $Cr(CO)_6$ (660 mg, 3.00 mmol) in Et_2O (500 mL) *via* syringe. The reaction mixture was stirred (1 h) followed by solvent removal. The obtained residue was treated, at −40 °C, with, in sequence, CH_2Cl_2 (50 mL), NMe_4-Cl (508 mg, 4.64 mmol), and 4-methoxybenzoyl chloride (465 μL, 3.44 mmol). After stirring (18 h), the solvent was removed, and hexanes−EtOAc (1:1, 50 mL) was added to the resulting brown solid residue. The open flask was put outside the chemistry building, and the slurry was oxidized in the sunlight, "air-oxidation", for 3 h. The colorless solution with a brown solid residue was filtered (Celite), and the solvents were removed. The crude product was purified by chromatography (hexanes−EtOAc, 19:1), affording **15** (112 mg, 0.51 mmol, 17%) as a colorless oil.

(*Z*)-1-Penten-1-yl 2,2-Dimethylpropanoate (16). Reaction of tetramethylammonium pentacarbonyl(1-oxopentyl)-chromate(1−) (**5**) (351 mg, 1.00 mmol) with 2,2-dimethylpropanoyl chloride (123 μL, 1.00 mmol) in CH_2Cl_2 (10 mL) at −40 °C, as described above, gave, after evaporation and short column chromatography (ethanol), **16** (83 mg, 0.49 mmol, 49%, Z/E = 6:1) as a colorless oil: IR (film) 2960, 2920, 2870, 1740 (CO), 1475, 1455, 1395, 1370, 1275, 1140 cm^{-1}; MS (EI) m/z 170 (M^+). Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66. Found: C, 70.89; H, 10.35.

***Z*-16:** from a 11:2 (Z/E) mixture; ^{1}H NMR (90 MHz) δ 7.01 (d, J = 7.2 Hz, 1 H), 4.89 (q, J = 7.3 Hz, 1 H), 2.13 (q, J = 7.4 Hz, 2 H), 1.41 (m, J = 7.7 Hz, 2 H), 1.26 (s, 9 H), 0.91 (t, J = 6.9 Hz, 3 H); ^{13}C NMR (22.5 MHz) δ 175.5, 134.4, 113.9, 38.8, 26.9 (3C), 22.2, 18.2, 13.5.

***E*-16:** partial spectra from a 11:2 (Z/E) mixture; ^{1}H NMR (90 MHz) δ 6.42 (dt, J = 12.5, 7.1 Hz, 1 H), 1.24 (s, 9 H); ^{13}C NMR (22.5 MHz) δ 135.7, 114.5, 26.3 (3C), 22.6.

Reaction of **5** (351 mg, 1.00 mmol) with 2,2-dimethylpropanoyl chloride (123 μL, 1.00 mmol) in CH_2Cl_2 (10 mL) at ambient temperature for 21 h, as described above, gave, after chromatography (pentane−Et_2O, 9:1), **16** (93 mg, 0.55 mmol, 55%, Z/E = 7.6:1) as a colorless oil.

Reaction of **5** (352 mg, 1.00 mmol) with 2,2-dimethylpropanoyl chloride (123 μL, 1.00 mmol) in CH_2Cl_2 (10 mL) at −40 °C in the presence of pyridine (81 μL, 1.00 mmol) gave, after evaporation and column chromatography (pentane), **16** (68 mg, 0.40 mmol, 40%, Z/E = 10:1) as a colorless oil.

2-Methyl-1-buten-1-yl 2,2-Dimethylpropanoate (17). Reaction of tetramethylammonium pentacarbonyl(1-oxo-2-methylbutyl)chromate(1−) (**6**)[45] (1.404 g, 4.00 mmol) with 2,2-dimethylpropanoyl chloride (493 μL, 4.00 mmol) in CH_2Cl_2 (60 mL) at −40 °C, as described above, gave, after evaporation and short column chromatography (ethanol), **17** (310 mg, 1.84 mmol, 46%, Z/E = 5:3) as a colorless oil. Spectral data from a 3:2 (Z/E) mixture: IR (neat) 2970, 2930, 2875, 1730, 1695, 1475, 1455, 1395, 1275, 1145, 1040, 1005 cm^{-1}; MS (EI) m/z 170 (M^+).

***Z*-17:** ^{1}H NMR (90 MHz) δ 6.89 (br s, 1 H), 2.01 (q, J = 7.8 Hz, 2 H), 1.68 (d, J = 1.0 Hz, 3 H), 1.25 (s, 9 H), 1.02 (t, J = 7.7 Hz, 3 H); ^{13}C NMR (22.5 MHz) δ 175.7, 129.9, 123.5, 38.8, 27.1 (3C), 22.7, 13.4, 12.0.

***E*-17:** ^{1}H NMR (90 MHz) δ 6.81 (m, 1 H), 2.14 (q, J = 7.4 Hz, 2 H), 1.63 (d, J = 1.5 Hz, 3 H), 1.25 (s, 9 H), 1.00 (t, J = 7.4 Hz, 3 H); ^{13}C NMR (22.5 MHz) δ 175.6, 129.5, 123.4, 38.8, 26.5 (3C), 22.3, 17.0, 11.4.

2-Methyl-1-buten-1-yl Acetate (18). To a −40 °C cold solution of tetramethylammonium pentacarbonyl(1-oxo-2-methylbutyl)chromate(1−) (**6**) (1.404 g, 4.00 mmol) in CH_2Cl_2 (60 mL) was added acetyl chloride (284 μL, 4.00 mmol), as described above, and the mixture gave, after evaporation and column chromatography (ethanol), **18** (110 mg, 0.86 mmol, 21%, Z/E = 5:3) as a colorless oil.[25a,46]

(*Z*)-3-Phenyl-1-propen-1-yl Acetate (19). Reaction of tetramethylammonium pentacarbonyl(1-oxo-3-phenylpropyl)-chromate(1−) (**7**)[47] (798 mg, 2.00 mmol) with acetyl bromide (142 μL, 2.00 mmol) in CH_2Cl_2 (40 mL) at −40 °C to ambient temperature (20 h), as described above, gave, after solvent removal at water aspirator pressure (0 °C) and chromatography (pentane−Et_2O, 8:2), **19** (92 mg, 0.52 mmol, 26%, Z/E = 17:1) as a faint yellow oil.[48]

Reaction of **7** (399 mg, 1.00 mmol) with acetyl chloride (71 μL, 1.00 mmol) and pyridine (81 μL, 1.00 mmol) in CH_2Cl_2 (25 mL) at −40 °C to ambient temperature (20 h), as described above, gave, after solvent removal at water aspirator pressure (0 °C) and chromatography (pentane−Et_2O, 9:1), **19** (69 mg, 0.40 mmol, 40%, Z/E = 40:1) as a faint yellow oil followed by $(CO)_5CrC_5H_5N$ (101 mg, 0.38 mmol, 38%) as yellow crystals.

(*Z*)-Hexen-1-yl Acetate (20). Reaction of tetramethylammonium pentacarbonyl(1-oxohexyl)chromate(1−) (**8**) (730 mg, 2.00 mmol) with acetyl chloride (142 μL, 2.00 mmol) in CH_2Cl_2 (50 mL) at −40 °C to ambient temperature (24 h), as described above, gave, after solvent removal at water aspirator pressure (0 °C) and chromatography (pentane−Et_2O, 9:1), **20** (88 mg, 0.62 mmol, 31%, Z/E = 19:1) as a faint yellow oil.[18]

(*Z*)-Hexen-1-yl pentanoate (21). Reaction of tetramethylammonium pentacarbonyl(1-oxohexyl)chromate(1−) (**8**) (730 mg, 2.00 mmol) with pentanoyl chloride (261 μL, 2.20 mmol) in CH_2Cl_2 (50 mL) at −40 °C to ambient temperature (24 h), as described above, gave, after solvent removal at water aspirator pressure (0 °C) and chromatography (pentane−Et_2O, 19:1), **21** (199 mg, 1.08 mmol, 54%, Z/E = 13:1) as a faint yellow oil.[18]

Reaction of **8** (365 mg, 1.00 mmol) with pentanoyl chloride (120 μL, 1.00 mmol) and pyridine (81 μL, 1.00 mmol) in CH_2Cl_2 (20 mL) at −40 °C to ambient temperature (20 h), as described above, gave, after solvent removal at water aspirator pressure (0 °C) and chromatography (pentane−Et_2O, 19:1), **21** (152 mg, 0.83 mmol, 83%, Z/E > 20:1) as a faint yellow oil followed by $(CO)_5CrC_5H_5N$ (120 mg, 0.45 mmol, 45%) as yellow crystals.

Cyclohexylidenemethanol Acetate (22). Reaction of tetramethylammonium pentacarbonyl(cyclohexylcarbonyl)-chromate(1−) (**9**) (1.51 g, 4.00 mmol) with acetyl chloride (285 μL, 4.00 mmol) in CH_2Cl_2 (40 mL) at −40 °C to ambient temperature (14 h), as described above, gave, after solvent removal at water aspirator pressure (0 °C) and chromatography (pentane−Et_2O, 19:1), **22** (402 mg, 2.61 mmol, 65%) as a colorless oil.[49]

(*Z*)-4-Chloro-1-buten-1-yl 4-Methoxybenzoate (23). Reaction of tetramethylammonium pentacarbonyl(cyclopropylcarbonyl)chromate(1−) (**10**)[20,24] (670 mg, 2.00 mmol) with 4-methoxybenzoyl chloride (272 μL, 2.01 mmol) in CH_2Cl_2 (20 mL) at −40 °C to ambient temperature, as described above (24 h), gave, after air-oxidation (16 h) and chromatography (pentane−Et_2O, 8:2) **23** (187 mg, 0.78 mmol, 39%, Z/E > 15:1) as a colorless oil:[50] IR (neat) 1721 cm^{-1}; ^{1}H NMR (90 MHz) δ 8.05 (d, J = 9.1 Hz, 2 H), 7.38 (d with further fine splitting, J = 6.4 Hz, 1 H), 6.96 (d, J = 9.1 Hz, 2 H), 5.04 (q, J = 6.6 Hz,

(43) The minor *E*-isomer could not be seen in the ^{1}H NMR spectra, but some of the ^{13}C NMR peaks were recorded: δ 134.0, 121.8, 114.3, 55.7, 29.5, 22.8.

(44) Nakamura, T.; Matsuyama, H.; Iyoda, M. *Chem. Lett.* **1994**, 1537.

(45) Montgomery, J.; Wieber, G. M.; Hegedus, L. S. *J. Am. Chem. Soc.* **1990**, *112*, 6255.

(46) *Z*-Isomer: Commercon, A.; Normant, J.; Villeras, J. *J. Organomet. Chem.* **1975**, *93*, 415.

(47) Söderberg, B. C.; Odens, H. H. *Organometallics* **1996**, *15*, 5080.

(48) Taguchi, T.; Morikawa, T.; Takigawa, T.; Yoshizawa, A.; Tawara, Y.; Kobayashi, Y. *Nippon Kagaku Kaishi* **1985**, *11*, 2177.

(49) Hurst, J. R.; Wilson, S. L.; Schuster, G. B. *Tetrahedron* **1985**, *41*, 2191.

(50) The *E*-isomer was not observed by ^{1}H or ^{13}C NMR.

1 H), 3.88 (s, 3 H), 3.61 (t, J = 6.9 Hz, 2 H), 2.76 (q, J = 6.9 Hz, 2 H); ^{13}C NMR (22.5 MHz) δ 164.0 (s), 163.0 (s), 136.3 (d), 132.1 (d, 2C), 121.4 (s), 113.9 (d, 2C), 109.3 (d), 55.47 (q), 43.6 (t), 28.3 (t). Anal. Calcd for $C_{13}H_{15}ClO_3$: C, 61.30; H, 5.94. Found: C, 61.49; H, 6.07.

(*Z*)-4-Chloro-1-buten-1-yl Acetate (24). Reaction of tetramethylammonium pentacarbonyl(cyclopropylcarbonyl)chromate(1−) (**10**) (335 mg, 1.00 mmol) with acetyl chloride (71 μL, 1.00 mmol) and pyridine (81 μL, 1.00 mmol) in CH_2Cl_2 (10 mL) at −40 °C to ambient temperature, as described above (21 h), gave, after chromatography (pentane−Et_2O, 9:1), **24** (36 mg, 0.36 mmol, 24%, Z/E > 20:1) as a pale yellow oil: IR (neat) 1759 cm^{-1}; ^{1}H NMR δ 7.13 (d, J = 6.3 Hz, 1 H), 4.93 (q, J = 6.9 Hz, 1 H), 3.54 (t, J = 6.9 Hz, 2 H), 2.63 (q with further fine splitting, J = 6.9 Hz, 2 H), 2.16 (s, 3 H); ^{13}C NMR δ 167.1 (+), 135.9 (−), 109.2 (−), 43.5 (+), 27.9 (+), 20.7 (−). Anal. Calcd for $C_6H_9ClO_2$: C, 48.50; H, 6.10. Found: C, 48.62; H, 6.20.

Ethenyl 4-Methoxybenzoate (2). Reaction of tetramethylammonium pentacarbonyl(1-oxo-2-(trimethylsilyl)ethyl)chromate(1−) (**11**)[24] (381 mg, 1.00 mmol) with 4-methoxybenzoyl chloride (141 μL, 1.04 mmol) and pyridine (81 μL, 1.00 mmol) in CH_2Cl_2 (10 mL) at −40 °C, as described above, gave, after column chromatography (pentane−Et_2O, 9:1), **2** (12 mg, 0.05 mmol, 5%) as a colorless oil.

1,1-Dideuterio-2-phenyl-1-iodoethane (38). To a 500 mL flask filled with argon were added 1,1-dideuterio-2-phenylethanol (**37**)[51] (2.54 g, 20.48 mmol), PPh_3 (21.32 g, 81.20 mmol), imidazole (5.53 g, 81.20 mmol), I_2 (15.49 g, 60.9 mmol), and toluene (180 mL). The resulting yellow-white suspension was stirred overnight at ambient temperature (23 h) followed by dropwise addition of $NaHCO_3$ (aq, saturated) over a 10 min period. Small portions of I_2 (s) were added until the organic layer had a persisting red color followed by small portions of sodium thiosulfate (s) until the color disappeared. The phases were separated, and the aqueous phase was extracted with toluene (2 × 90 mL). The combined organic phase was washed with brine (50 mL), dried ($MgSO_4$), and filtered. Solvent removal at reduced pressure gave a yellow-white solid residue. The residue was purified by chromatography (hexanes), affording **38** (3.68 g, 15.73 mmol, 79%) as a colorless oil.[51]

(*Z*)-2-*d*-4-Phenyl-1-propen-1-yl Acetate (40). Acetyl chloride (142 μL, 2.00 mmol) was added dropwise *via* syringe to a −40 °C cold slurry of tetramethylammonium pentacarbonyl-(2,2-dideuterio-1-oxo-3-phenylpropyl)chromate(1−) (**39**) (1.00 g, 2.49 mmol)[39] in CH_2Cl_2 (25 mL). The reaction mixture was allowed to reach ambient temperature slowly. After 20.5 h, the formed faint yellow solution containing a yellow precipitate was filtered (Celite), and the filter was washed with pentane (10 mL). Removal of solvents gave a pale yellow-green oil containing $Cr(CO)_6$ crystals. The crude product was purified by chromatography (hexanes) to give **40** (152 mg, 0.86 mmol, 34%) as a colorless oil after solvent removal. An 11:1 ratio of Z/E-**40** was obtained having the following spectral data: ^{1}H NMR δ 7.4−7.1 (m, 6 H), 3.43 (s, 2 H), 2.10 (s, 3 H); ^{13}C NMR δ 168.0 (+), 140.0 (+), 134.6 (−), 128.5 (−), 128.3 (−), 126.1 (−), 112.2 (t, J = 98.8 Hz, +), 30.6 (+), 20.7 (−); IR (neat) 1750, 1265, 738 cm^{-1}. Partial spectra of the *E*-isomer: ^{1}H NMR (270 MHz) δ 3.34 (s), 2.12 (s); MS (EI) m/z 177 (M^+). Anal. Calcd for $C_{11}H_{11}DO_2$: C, 74.58; H + D, 6.78. Found: C, 74.69; H + D, 6.95.

Reaction of **39** (401 mg, 1.00 mmol) with acetyl chloride (71 μL, 1.00 mmol) and pyridine (81 μL, 1.00 mmol) in CH_2Cl_2 (25 mL) at −40 °C to ambient temperature (20 h), as described above, gave, after solvent removal at water aspirator pressure (0 °C) and chromatography (pentane−Et_2O, 9:1), **40** (58 mg, 0.33 mmol, 33%, Z/E > 35:1) as a faint yellow oil followed by a quantitative amount of $(CO)_5CrC_5H_5N$ as yellow crystals.

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(51) von Loibner, H.; Zbiral, E. *Helv. Chim. Acta* **1976**, *59*, 2100.