Lithium and Tetramethylammonium Pentacarbonyl(1-oxidoethylidene)chromate(0) ↔ Acetylpentacarbonylchromate(0) as Acetyl Anion Equivalents for Conjugate Addition Reactions with Electron Deficient Alkenes

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Received June 17, 1994[⊗]

Thermal and photolytic reactions of lithium pentacarbonyl(1-oxidoethylidene)chromate(0) (**1**) and tetramethylammonium pentacarbonyl(1-oxidoethylidene)chromate(0) (**22**) with various electron deficient alkenes were investigated. The acyl metalates were found to be formally an acetyl anion equivalent, adding in a Michael fashion. Depending on reaction conditions, the products were found to be derived from the addition of 1 equiv of pentacarbonyl(1-oxidoethylidene)chromate(0) to either 1, 2, or 3 equiv of the initial alkene. Conditions were found affording exclusively or predominantly 1:1 addition and, conversely, 2:1 addition.

Introduction

The search for synthetically useful acyl anion equivalents has been extensive.[1] Several routes toward these synthons involve the reaction of "R-" with carbon monoxide, either metal-bound or free. Seyferth has done extensive work developing acyl anions, both directly, by reaction of alkyllithium reagents with CO, and indirectly, by using acylcuprates as equivalents for the parent anion.[2] Semmelhack has used $Fe(CO)_5$ and alkyllithiums to generate acyl anion equivalents.[3] An interesting method has been developed by Thomas that relies upon reaction of tetracarbonyliron complexes of α,β-unsaturated esters with alkyllithiums to obtain formal Michael addition products.[4] Alkyl pentacarbonyl manganese complexes react, under high CO pressure (2–6 kbar), with α,β-unsaturated carbonyl compounds to give, after photolytic cleavage, formal Michael adducts.[5] Alkyllithiums (methyl or n-butyl) in the presence of either $Ni(CO)_4$[6] or $Co(PPh_3)(NO)(CO)_2$[7] undergo conjugate addition reaction of the *in situ* formed acyl anion with α,β-unsaturated carbonyl compounds to give 1,4-dicarbonyl compounds. Corey and Hegedus suggested three possible mechanistic pathways: (1) preliminary electron transfer, (2) direct acyl anion transfer, or (3) cycloaddition of the acyl anion in a fashion similar to alkoxy carbenes. This last mechanistic possibility led us to consider the reactions of anionic 1-oxidoalkylidene group VI metal complexes with a series of α,β-unsaturated carbonyl substrates. We describe herein the results of our study of the reaction of lithium (**1**) and tetramethylammonium (**22**) pentacarbonyl(1-oxidoethylidene)chromate(0) [which is referred to as acetylpentacarbonylchromate(0) ion] with various electron deficient alkenes. Contrasting and complementary results arise from the use of thermally vs photochemically activated reactions.

Results and Discussion

Previous work in one of our laboratories[8] has revealed some advantages of using anionic complexes such as **1** as carbene equivalents. This is noteworthy since **1** may be considered both as an acyl metalate and as a Fischer carbene complex, the latter bearing a particularly electron-rich donor atom. A variety of these complexes can be generated using both alkyllithium and Grignard reagents.[9] These complexes can then be reacted with alkynes *in situ* affording, upon work up, alkyne/carbene adducts together with a substantial portion of recovered chromium hexacarbonyl.[8a] We were originally inter-

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[⊗] Abstract published in *Advance ACS Abstracts,* September 1, 1994.

(1) For a compilation of references of R-functional acyl anion synthons RCO-, see: a) Hase, T. A.; Koskimies, J. K. *Aldrichimica Acta* **1982**, *15*, 35. b) Ager, D. J. In *Umpoled Synthons*: Hase, T. A., Ed.; Wiley Interscience: New York, 1987, p 19.

(2) a) Seyferth, D.; Weinstein, R. M.; Wang, W. L. *J. Org. Chem.* **1983**, *48*, 1144. b) Weinstein, R. M.; Wang, W.-L.; Seyferth, D. *J. Org. Chem.* **1983**, *48*, 3367. c) Seyferth, D.; Weinstein, R. M.; Wang, W.-L.; Hui, R. C. *Tetrahedron Lett.* **1983**, 4907. d) Seyferth, D.; Wang, W.-L.; Hui, R. C. *Tetrahedron Lett.* **1984**, 1651. e) Seyferth, D.; Hui, R. C. *J. Am. Chem. Soc.* **1985**, *107*, 4551.

(3) a) Semmelhack, M. F.; Tamura, R. *J. Am. Chem. Soc.* **1983**, *105*, 6750. b) Semmelhack, M. F.; Tamura, R.; Schnatter, W.; Springer, J. *J. Am. Chem. Soc.* **1984**, *106*, 5363.

(4) a) Rakshit, D.; Thomas, S. E. *J. Organomet. Chem.* **1987**, *333*, C3. b) Thomas, S. E. *J. Chem. Soc., Chem. Commun.* **1987**, 226.

(5) DeShong, P.; Sidler, D. R.; Rybczynski, P. J.; Slough, G. A.; Rheingold, A. L. *J. Am. Chem. Soc.* **1988**, *110*, 2575 and references cited therein.

(6) a) Corey, E. J.; Hegedus, L. S. *J. Am. Chem. Soc.* **1969**, *91*, 4926. b) Semmelhack, M. F.; Keller, L.; Sato, T.; Spiess, E. *J. Org. Chem.* **1982**, *47*, 4382.

(7) Hegedus, L. S.; Perry, R. J. *J. Org. Chem.* **1985**, *50*, 4955.

(8) a) Hoye, T. R.; Rehberg, G. M. *J. Am. Chem. Soc.* **1990**, *112*, 2841. b) Hoye, T. R.; Rehberg, G. M. *Organometallics* **1990**, *9*, 3014. c) See also: Katz, T. J.; Yang, G. X.-Q. *Tetrahedron Lett.* **1991**, *32*, 5895.

(9) Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissl, F. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; Verlag Chemie: Deerfield Beach, FL, 1984.

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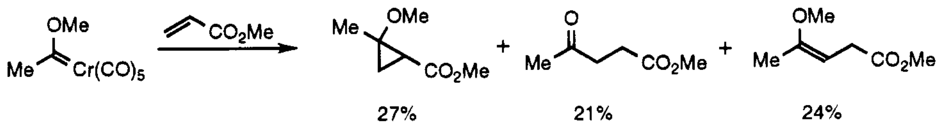
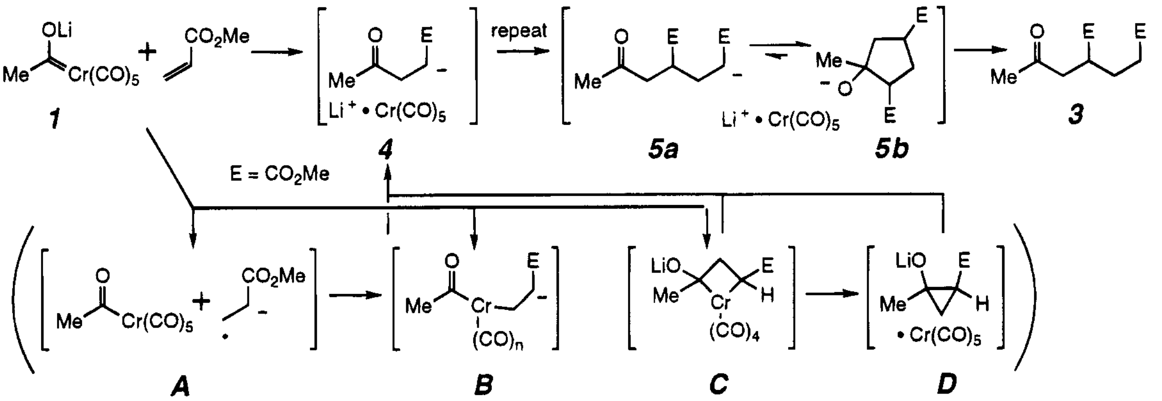
Scheme 1



Scheme 2



ested in the possibility of using these anions for the formation of "push-pull" activated cyclopropanes. Fischer and Reissig have shown[10] that alkoxy-substituted carbene complexes react with electron deficient alkenes to give "push-pull" cyclopropanes in good yields.[11] We have described[12] an example of a similarly activated enamino cyclopropyl ester that fragmented via a presumed zwitterionic intermediate under the conditions of its formation.

Thermal Reactions. In our initial experiment (entry 1 in Table 1), lithium pentacarbonyl(1-oxidoethylidene)chromate(0) (**1**) was prepared *in situ* by the reaction of chromium hexacarbonyl with methyllithium in tetrahydrofuran (THF). Methyl acrylate was then added to the homogeneous solution, and the resulting mixture was heated at reflux under nitrogen for 2 h. Air oxidation of metal-containing byproducts followed by silica gel chromatography resulted in the isolation of methyl 4-oxopentanoate (**2**) in 47% yield along with a minor amount (7%) of dimethyl 2-(2-oxopropyl)-pentanedioate (**3**) arising from the incorporation of a second molecule of methyl acrylate. Use of a larger excess of acrylate (10 equiv) and refluxing the reaction mixture for 16 h resulted in a substantial preference for the 2:1 adduct **3** (entry 2). Production of the 2:1 adduct **3** foreshadowed a number of the events to follow. This result differs from the generation of simple 1:1 adducts when $(RCO)Ni(CO)_3{}^{-}$[6a] or $(RCO)MnCp'(CO)_3{}^{-}$[8b] are reacted with acrylate and other enones and enoates. Formal Michael addition products have been isolated from reaction of alkoxy and amino-substituted Fischer carbenes with electron deficient alkenes, albeit usually in low yield.[13] For alkoxy-substituted carbenes, the Michael addition products were shown to arise from Lewis acid cleavage of "push-pull" activated cyclopropanes, the principle product of these reactions (Scheme 1).

Several mechanistic formalisms can be entertained for the formation of 1:1 and 2:1 adducts, the latter of which is formally the product of a double Michael reaction. All mechanisms logically involve species like the 1:1 and 2:1 adduct ester enolate anions **4** and **5a** followed by protonation. The former could be generated by a variety of pathways analogous to those originally suggested by Corey and Hegedus[6a] (see parentheses in Scheme 2). Thus, reaction of methyl acrylate with **1** via electron transfer, direct 1,4-addition of chromium acylate, or formal [2 + 2] addition to methyl acrylate, forming the intermediates **A**, **B**, or **C**, respectively, are all plausible initial steps in this reaction. The exact timing of subsequent steps is hard to determine due to the mechanistic complexity. The ester enolate anion **4** can be produced by reductive elimination within **B** or ring fission of **C** or **D**, the latter formed by reductive elimination in **C**. The mechanistic picture is further complicated by several possible routes to the 2:1 product **5** via, for example, Michael reaction of **B** with a second molecule of methyl acrylate or insertion of methyl acrylate into a carbon–chromium bond in **B** or **C**. It should be noted that the source of the proton in these reactions is presently not known. An intriguing question, of course, is why the event stops at the point of the 2:1 adduct rather than continue to oligomerize, but a definitive answer is not at hand. A referee has suggested the possible intervention of the aldolate **5b** as a resting point until proton quench leading to **3**.

Reaction of the substituted acrylate derivatives methyl crotonate and methyl methacrylate with **1** was also examined. After refluxing in THF 1–2 h, the 1:1 adducts **6** and **9** were isolated in 16 and 41% yields, respectively (Table 1, entries 4 and 8). In addition a set of enol-lactones (or butenolides) representing 2:1 (**7** and **10**) and 3:1 (**8**) adducts between the acylchromate anion **1** and the appropriate acrylate was isolated. As expected, longer reaction times and/or more starting crotonate or methacrylate esters again biased the product ratios away from the simple 1:1 adducts (entries

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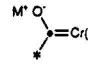
(10) For examples, see: a) Wienand, A.; Reissig, H.-U. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1129. b) Wienand, A.; Reissig, H.-U. *Tetrahedron Lett.* **1988**, *29*, 2315. c) Buchert, M.; Reissig, H.-U. *Tetrahedron Lett.* **1988**, *29*, 2319. d) Dötz, K. H.; Fischer, E. O. *Chem. Ber.* **1972**, *105*, 1356. e) Fischer, E. O.; Dötz, K. H. *Chem. Ber.* **1970**, *103*, 3966. f) Fischer, E. O.; Dötz, K. H. *Chem. Ber.* **1970**, *103*, 1273.

(11) For a review of push-pull cyclopropanes, see: Reissig, H.-U. *Top. Curr. Chem.* **1988**, *144*, 73.

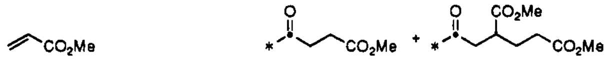
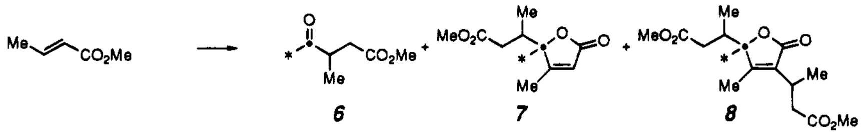
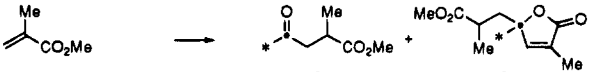
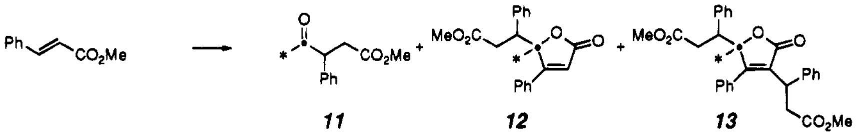
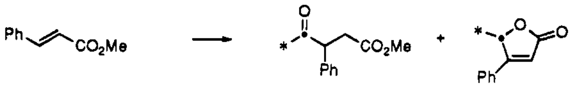
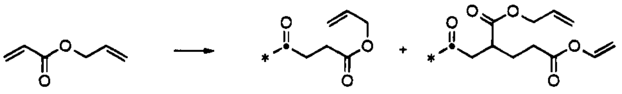
(12) Hoye, T. R.; Rehberg, G. M. *Organometallics* **1989**, *8*, 2070.

(13) a) Sierra, M. A.; Söderberg, B. C.; Lander, P. A.; Hegedus, L. S. *Organometallics* **1993**, *12*, 3769. b) Buchert, M.; Reissig, H.-U. *Chem. Ber.* **1992**, *125*, 2723. c) Wienand, A.; Reissig, H.-U. *Chem. Ber.* **1991**, *124*, 957. d) Herndon, J. W.; Turner, S. U. *J. Org. Chem.* **1991**, *56*, 286. e) Wienand, A.; Reissig, H.-U. *Organometallics* **1990**, *9*, 3133.

Table 1. Reaction of Lithium and Tetramethylammonium Pentacarbonyl(1−oxidoethylidene)chromate(0) (1 and 22) with α,β-Unsaturated Esters under Thermal Conditions[a]



1 M = Li
22 M = Me$_4$N

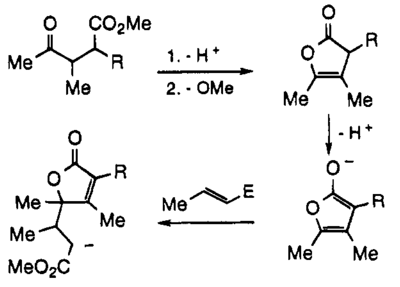
Entry	Enoate Substrate # Equivs	Time (h)	Chromate Counterion	Product(s) Yield (%)		
				**2**	**3**	
1	2.1	2	Li$^+$	47 %	7%	
2	10.0	16	Li$^+$	4 %	32 %	
3	1.1	24	Me$_4$N$^+$	79 %	0 %	
				**6**	**7**	**8**
4	2.0	2	Li$^+$	16 %	10 %	2 %
5	5.0	2	Li$^+$	11 %	29 %	4 %
6	5.0	17	Li$^+$	6 %	31 %	10 %
7	2.0	24	Me$_4$N$^+$	40 %	8 %	0 %
				**9**	**10**	
8	2.1	1	Li$^+$	41 %	8%	
9	10.0	16	Li$^+$	0 %	37 %	
				**11**	**12**	**13**
10	1.1	17	Li$^+$	24 %	5 %	4 %
				**11**	**23**	
11	1.1	24	Me$_4$N$^+$	13 %	16 %	
				**15**	**16**	
12	2.1	2	Li$^+$	38 %	5 %	

[a] Yields represent isolated materials following MPLC on silica gel. The starred (*) and bulleted (•) atoms represent those arising from the methyl carbon and carbene carbon, respectively, of the initial complex **1** or **22**.

5, 6, and 9). However, in contrast to the simple 2:1 addition products structurally analogous to **3**, the butenolides **7**, **8**, and **10** were isolated after prolonged heating. The probable pathway for the formation of butenolides such as **7** and **8** involves enol-lactonization after either 1:1 or 2:1 addition, deprotonation to the relevant butenolide anion, and subsequent Michael addition to a second (or third) equivalent of crotonate exclusively at the γ position (Scheme 3).[14]

Reaction of methyl cinnamate with the lithium chromate **1** gave a similar product pattern of 1:1, 2:1, and 3:1 adducts after 17 h (**11**–**13**, Table 1, entry 10). Once again greater amounts of butenolide formation accompanied the use of larger amounts of enoate and longer reaction time.

Scheme 3



R = H or -CHMeCH$_2$CO$_2$Me

Several experiments were conducted in an attempt to learn more about the nature of the intermediate anions formed upon reaction of **1** with various α,β-unsaturated esters. An attempt to trap the intermedi-

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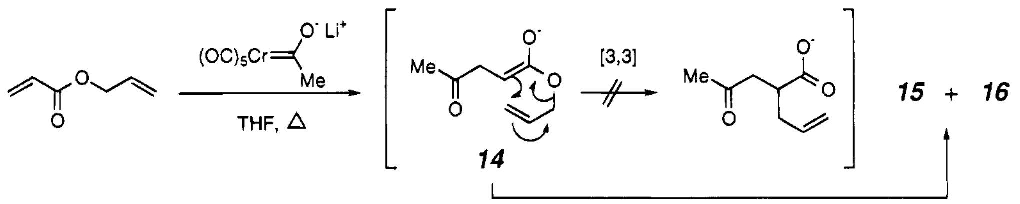
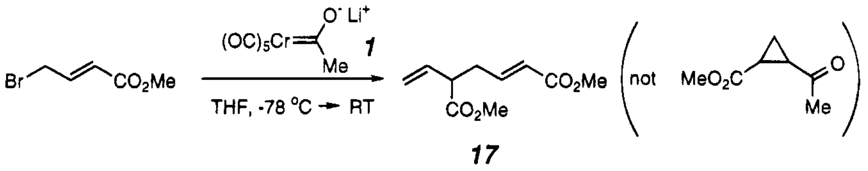
(14) Kraus, G. A.; Roth, B. *Tetrahedron Lett.* **1977**, 3129.

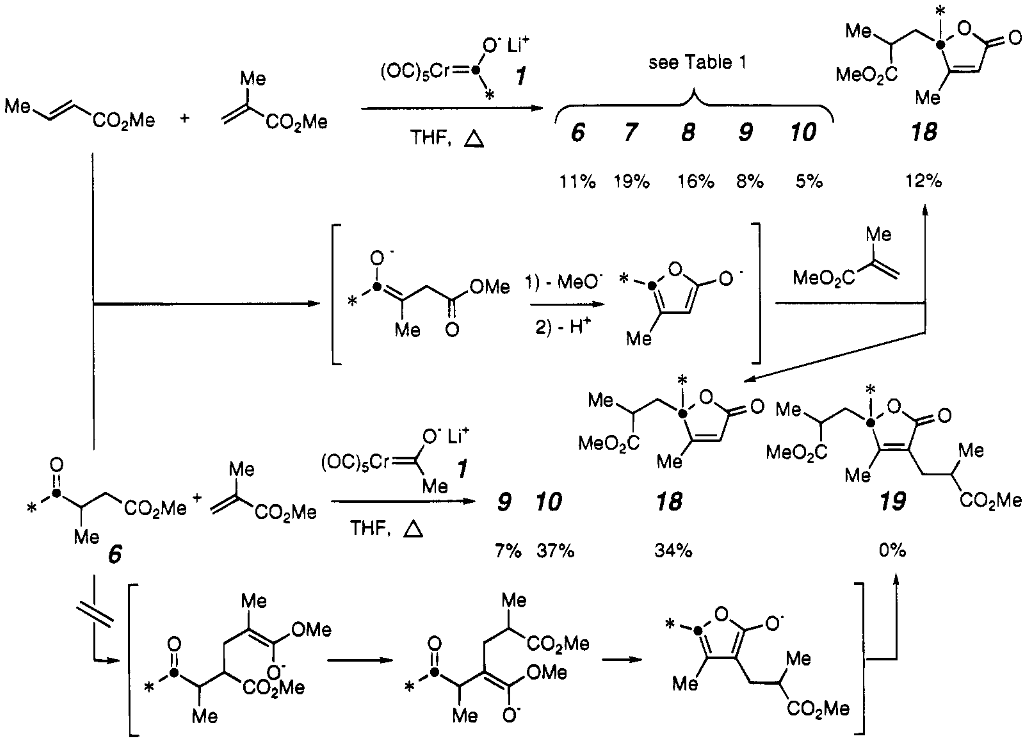
Scheme 4



Scheme 5



Scheme 6



ate derived from **1** and methyl acrylate (**4**, Scheme 2) with methyl iodide was unsuccessful. In a different trapping experiment, allyl acrylate was reacted with **1**. In this case the possible intermediate enolate ion **14** is appropriately arrayed for an Ireland–Claisen ester enolate rearrangement (Scheme 4).[15] However, even though this reaction was performed in refluxing THF, no products resulting from this rearrangement were observed. Instead only the 1:1 and 2:1 products, **15** and **16**, respectively, from addition of allyl acrylate and the acyl anion were formed (Table 1, entry 12).

Methyl 4-bromocrotonate was also subjected to the reaction with **1** in anticipation that the intermediate anion formed after the addition of the acyl anion might displace the bromide in an intramolecular S_N2 fashion to give a substituted cyclopropane. This exothermic reaction gave, however, as the sole product the reductively coupled dienedioate **17** in 81% yield (Scheme 5).[16] The results obtained from the three experiments described above either argue against the ester enolate anion **4** as a likely intermediate in these reactions or are a result of alteration of normal ester enolate reactivity by the remaining chromium pentacarbonyl residue.

Reaction of lithium pentacarbonyl(1-oxidoethylidene)-chromate(0) (**1**) with equal molar ratios of methyl acrylate and methyl crotonate resulted in formation of only the acrylate adduct **3** with no incorporation of the crotonate observed (by GC analysis). Similar results were seen when methacrylate was used in competition with acrylate (GC). However, as summarized in Scheme 6, competitive reaction of **1** with equimolar amounts of crotonate and methacrylate gave rise to a product mixture that indicated more comparable rates of incorporation for this pair of enoates. A slight (~4:1)

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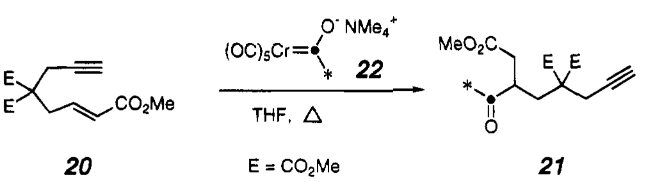
[15] For recent examples and pertinent references; see: Ireland, R. E.; Wipf, P.; Xiang, J.-N. *J. Org. Chem.* **1991**, *56*, 3572.

[16] For related couplings of allylic bromides in the presence of Co(PPh$_3$)(NO)(CO)$_2$, see: reference 7.

Scheme 7



preference for initial addition of **1** to crotonate over methacrylate was observed. Furthermore, a new mixed butenolide **18**, into which 1 equiv each of methyl crotonate and methyl methacrylate had been incorporated, was isolated. When 3-methyl-4-oxopentanoic acid methyl ester (**6**, the 1:1 adduct of crotonate and the acyl anion) was included from the outset in a reaction between **1** and methyl methacrylate, the butenolide product **18** again was obtained. Thus, the 1:1 adduct of crotonate underwent enol-lactonization to a butenolide and subsequently added methacrylate in the 5-position. However, the butenolide **19**, which would have been derived from addition of methacrylate to the anion of the 4-oxopentanoate **6** before enol-lactonization, was not observed. This implies that the *neutral* 1:1 adduct can be an intermediate on the pathway to the 2:1 butenolides like **7** and **18**, but that it is not on the pathway to the 3:1 butenolides like **8** or **19**. This is consistent with highly selective initial formation of a ketone rather than ester enolate from **6**.

Use of tetramethylammonium pentacarbonyl(1-oxidoethylidene)chromate(0) (**22**) in place of the lithium complex gave a slower but more selective reaction with electron deficient alkenes. Reaction of **22** with 1.1 equiv of methyl acrylate at reflux in THF for 24 h gave the 1:1 adduct **2** in 79% yield (Table 1, entry 3). No 2:1 adduct was observed. Methyl crotonate gave mainly the 1:1 product **6** upon reaction with **22** together with a small amount of the 2:1 product **7** (entry 7). Neutral Fischer carbene complexes generally react with the sterically more accessible alkynes before alkenes. However, when the enyne triester **20** was reacted with **1**, the major product was the result of acyl addition to the enoate to give the simple 1:1 adduct **21** (Scheme 7). This result suggests that electronic factors can override the steric biases in the reactions of the chromate anions like **1** and **22** and/or that the reaction of these anions with enoates is mechanistically distinct from the generally accepted pathways for neutral Fischer carbenes. Also in contrast to its reaction with the lithium complex **1**, methyl cinnamate gave, upon reaction with **22**, only the 1:1 adduct together with the butenolide **23** (entry 11). A much slower reaction was observed and some methyl cinnamate was recovered unchanged.

We have identified a number of limitations to this reaction. It has not been possible to generate addition products from these anionic Fischer carbenes to trisubstituted enoates. Thus, attempted reactions of **1** with ethyl tiglate, ethyl 3,3-dimethylacrylate, and methyl 3-methoxycrotonate as well as with methyl furoate all resulted in the recovery of starting alkene. Although the alkene substrate was consumed, the thermal reaction of **1** with acrylonitrile or 2-cyclohexen-1-one did not lead to recognizable products. Furthermore, addition of methylmagnesium iodide to chromium hexacarbonyl in THF, presumably forming a magnesium iodide acylchromate, followed by reaction with methyl crotonate at reflux, gave a complex mixture of products, demonstrating the importance of the cation of the reaction outcome.

Photolytic Reactions. Loss of one of the chromium bound carbonyl ligands is a likely initial event within the pentacarbonyl(1-oxidoethylidene)chromate(0) salts, enabling the subsequent coordination of the substrate. This can be achieved either by heating, as above, or by irradiation.[17] Thus, photolysis through Pyrex with a 450 W Hanovia lamp of a THF solution of the tetramethylammonium chromate **22** in the presence of 2.0 equiv of methyl crotonate gave the 1:1 adduct **6** in 63% yield together with 2-ethylidene-3-methylpentanedioic acid dimethyl ester (**24**, 36%, Scheme 8). No trace of 2:1 or 3:1 products was seen. The formation of the dimer **24** can be somewhat diminished (7%) by reducing the amount of methyl crotonate to 1.1 equiv, but the yield of **6** is also reduced (43%). The dimer **24** and related products have been observed by reaction of acrylic acid ester derivatives with a number of reagents,[18a] and it was isolated as early as 1900 by von Pechmann.[18b]

Photolytic reaction of **22** with methyl crotonate (2.0 equiv) under a carbon monoxide atmosphere (6 atm) produced the 1:1 adduct **6** in 57% yield, but surprisingly the formation of the dimer **24** was totally suppressed, suggesting the intermediacy of some type of chromium species in the formation of the latter. Pressurizing the reaction vessel with carbon monoxide has the added advantage that chromium hexacarbonyl can be readily recovered from the reaction mixture and reused.

It was recently reported that irradiation of a catalytic amount of bis[1,2-bis[(dimethylphosphino)ethane]iron dihydride [$FeH_2(dmpe)_2$] in the presence of methyl crotonate gave **24**.[19] Thus, the dimerization of methyl crotonate during reaction with **22** may be catalyzed or mediated by an analogous chromium hydride species. The reactive "catalyst" for this dimerization reaction is apparently not formed upon irradiation of the lithium complex **1** in the presence of methyl crotonate. No dimerization product was isolated in this experiment, but both the 1:1 and 2:1 butenolide adducts **7** and **8** were obtained in 15 and 46%, respectively, after 24 h. This also clearly illustrates the influence of the counterion on the reaction, since selective formation of **6** was observed using tetramethylammonium in place of lithium. The first addition step in the photochemical reaction may well parallel that of the thermal reaction. The observed higher selectivity, in the case of **22**, is perhaps largely due to the tetramethylammonium counterion.

Several additional electron deficient alkenes form Michael-type addition products when reacted with tetramethylammonium pentacarbonyl(1-oxidoethylidene)chromate(0) under photolytic conditions (Table 2). Pure products were obtained in most cases after air oxidation followed by filtration through Celite of the crude reaction mixtures, thus simplifying the procedure for their preparation. 3-Buten-2-one and 2-cyclopenten-1-one

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[17] Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587.

[18] a) Shabtai, J.; Ney-Igner, E.; Pines, H. *J. Org. Chem.* **1981**, *46*, 3795 and references cited therein. b) von Pechmann, H. *Chem. Ber.* **1900**, *33*, 3323.

[19] Komiya, S.; Oyasato, N.; Furukawa, T. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 4078.

Scheme 8

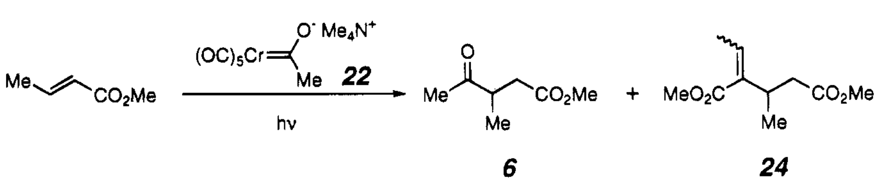
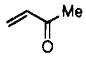
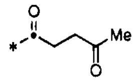
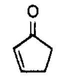
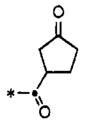
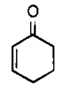
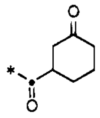
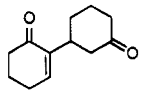
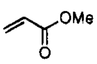
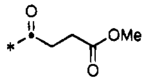
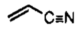
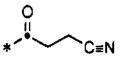
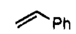
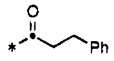
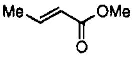
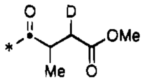
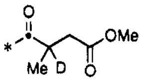


Table 2. Reaction of Tetramethylammonium (1-Oxidoethylidene)pentacarbonylchromate(0) (22) with Electron Deficient Alkenes under Photochemical Conditions[a]

Entry	Alkene Substrate	$\xrightarrow{22}$ Product(s), Yield (%)
1		 25 75%
2		 26 96%
3		 27 16%  28 45%
4		 2 33%
5		 29 38%
6		 30 6%
7		 31 30%  32 30%

[a] Yields represent isolated materials following MPLC on silica gel. The starred (*) and bulleted (•) atoms represent those arising from the methyl carbon and carbene carbon, respectively, of the initial complex **1** or **22**.

gave excellent yields of the acylated products **25** and **26** (entries 1 and 2, respectively). Furthermore, in contrast to the thermal reaction of the lithium complex, the photolytic reaction of **22** with cyclohexenone generated some of the acetyl addition adduct **27**. However, the major product was the dimer of cyclohexenone, **28**.

When this reaction was performed under carbon monoxide (4 atm), formation of the enone dimer was not suppressed as had been observed for methyl crotonate. At present, we do not know why only some alkenes give rise to dimerization products during the photochemical reaction. Methyl acrylate gave a substantially lower yield (33%) of the 1:1 adduct **2** when irradiated with the tetramethylammonium complex **22** compared to its thermal reaction with **22**. 4-Oxovaleronitrile (**29**), also not observed from reaction of acrylonitrile and **1**, was obtained in modest yield (entry 5 in Table 2). Finally, even the relatively nonactivated alkene, styrene, produced the 1:1 addition product 4-phenyl-2-butanone (**30**), although in a very low yield (entry 6). Note that no oligomeric products such as **7** or **8** were observed either in the crude reaction mixture (^{1}H NMR) or after purification in any of the photochemical reactions reported in Table 2.

The reaction of **22** with methyl crotonate in tetrahydrofuran in the presence of deuterium oxide gave the two deuterated products **31** and **32** as an inseparable 1:1 mixture (entry 7). The formation of both labeled regioisomers is suggestive of rapidly equilibrating anionic enolate intermediates. The same two products were obtained in the same ~1:1 ratio when the reaction was performed in acetone-d_6 albeit in lower yield (15%).

The influence of the solvent of the photolytic reaction of **22** with methyl crotonate was briefly studied. Yields of 4-oxopentanoic acid methyl ester (**2**) for the following solvents were: ethyl acetate (66%), tetrahydrofuran (63%), acetonitrile (53%), dichloromethane (43%), acetone (38%), diethyl ether (23%), and benzene (13%). No product was formed in hexanes.

We have not been able to obtain any addition products from photochemical reaction of tetramethylammonium pentacarbonyl(1-oxidoethylidene)chromate(0) (**22**) with methyl sorbate or methyl propiolate; both were recovered unchanged after 24 h of irradiation. Furthermore, although completely consumed, the enals acrolein and cinnamaldehyde as well as 1,4-benzoquinone, crotonic acid, and methyl cinnamate gave no isolable products, the last substrate in contrast to its thermal reactions with the complexes **1** and **22**. Furthermore, no product was isolated from divinyl sulfoxide, a result not surprising in light of the known ability of sulfoxides to oxidize the metal–carbon double bond of Fischer carbenes to an oxygen–carbon double bond.[20]

Summary. The reaction of pentacarbonyl(1-oxidoethylidene)chromate salts with electron deficient alkenes extends the use of the anionic carbene complexes beyond that usually associated with the neutral carbene complexes. By proper choice of either lithium or tetramethylammonium pentacarbonyl(1-oxidoethylidene)chromate(0) and the use of thermal versus photolytic reaction conditions, the product distribution can be substantially altered. The tetramethylammonium complex selectively, either under photolytic or thermal reaction conditions, affords formal 1:1 addition products of an acyl anion to electron deficient alkenes. The corresponding lithium salt also gives 1:1 addition products under thermal conditions using equimolar amounts of alkenes together with short reaction times. Further studies of other pentacarbonyl(1-oxidoalkylidene)chromate(0) salts as acyl anion synthons are presently underway in our laboratories.

Experimental Section

General Methods. THF and diethyl ether were distilled prior to use from sodium benzophenone ketyl. The hexanes and EtOAc used as chromatographic solvents were distilled at atmospheric pressure. All other reagents were used as

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[20] For oxidations using DMSO, see: a) Wulff, W. D.; Anderson, B. A.; Toole, A. J. *J. Am. Chem. Soc.* **1989**, *111*, 5485. b) Chan, K. S.; *J. Chem. Soc., Perkin Trans. 1* **1991**, 2602. For one example employing phenyl vinyl sulfoxide, see ref. 12a.

received unless otherwise indicated. Triester **21**[21] and tetramethylammonium pentacarbonyl(1-oxidoethylidene)chromate(0)[22] (**22**) were prepared according to literature procedures. All reactions involving anion chemistry were carried out under an inert atmosphere of either nitrogen or argon in flame-dried glassware. MPLC refers to medium pressure liquid chromatography using hand packed silica gel (230–400 mesh) columns and TLC or refractive index detection. The TLC plates were visualized either under UV light or by oxidation with a solution of phosphomolybdic acid in absolute ethanol (5 g per 100 mL). All NMR spectra were recorded in CDCl$_3$ using tetramethylsilane (0.00 ppm, ^{1}H NMR and ^{13}C NMR) or CDCl$_3$ (77.00 ppm ^{13}C NMR) as internal standards. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ.

General Procedure A: In Situ Formation and Reaction of Lithium Pentacarbonyl(1-oxidoethylidene)chromate(0) (1) with Electron Deficient Alkenes under Thermal Conditions. To a slurry of chromium hexacarbonyl (0.5 M in THF) in a threaded, septum-capped, culture tube under a N$_2$ or Ar atmosphere was added dropwise methyllithium via syringe at rT. The reaction mixture became homogeneous and assumed a dark, brown-black appearance within 10 min. The α,β-unsaturated compound was added via syringe, the septum was replaced by a Teflon-lined cap, and the reaction mixture was heated at 75 °C (external bath temperature). The crude reaction mixture was opened to the air at ambient temperature for ~1 h and passed through a plug of SiO$_2$ (EtOAc elution), and the solvent was removed on a rotary evaporator at water aspirator pressure. The resulting organics were purified by MPLC (hexanes–EtOAc) to provide the products in yields stated based on Cr(CO)$_6$.

4-Oxopentanoic Acid, Methyl Ester (2), and 2-(2-Oxopropyl)pentanedioic Acid, Dimethyl Ester (3). Prepared by the general procedure A using 0.220 g (1.0 mmol) of chromium hexacarbonyl, 714 μL (1.05 mmol) of methyllithium, and 0.185 g (2.1 mmol) of methyl acrylate. The reaction mixture was heated for 2 h, and the organics were purified by MPLC (hexanes:EtOAc, 3:1) affording 61 mg (47%) of **2** and 15 mg (7%) of **3** as colorless oils. Spectral data for **2** were in complete accord with literature values.[23] Spectral data for **3**. IR (neat): 2950, 2925, 1735, 1420, 1340, 1260, 1210, 1190, 1010 cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 3.67 (s, OMe, 3H), 3.64 (s, OMe, 3H), 3.02 (m, $\sum J$'s = 27.3 Hz, H2, 1H), 2.74 (dd, J = 9.5 and 16.8 Hz, H1'a, 1H), 2.35 (dd, J = 4.6 and 16.8 Hz, H1'b, 1H), 2.30 (t, J = 7.7 Hz, H4, 2H), 2.25 (s, H3', 3H), 1.97 (qd; J = ~7.4, ~7.4, ~7.4, and 14.0 Hz; H3a, 1H), 1.55 (qd; J = ~7.2, ~7.2, ~7.2, and 14.5 Hz; H3b, 1H). ^{13}C NMR (CDCl$_3$, 75 MHz): δ 210, 173.0, 172.4, 51.8, 51.7, 46.9, 34.9, 31.1, 29.4, 26.0. Anal. Calcd for $C_{10}H_{16}O_5$: C, 55.55; H, 7.45. Found: C, 55.56; H, 7.21.

3-Methyl-4-oxopentanoic Acid, Methyl Ester (6), 4,5,α-Trimethyl-2(5*H*)furanone-5-propanoic Acid, Methyl Ester (7), and 4,5,α,α′-Tetramethyl-2(5*H*)furanone-3,5-dipropanoic Acid, Dimethyl Ester (8). Prepared by the general procedure A using 0.220 g (1.0 mmol) of chromium hexacarbonyl, 0.75 mL (1.05 mmol) of methyllithium, and 0.212 mL (2.0 mmol) of methyl crotonate. The reaction mixture was heated for 2 h, and the resulting organics purified by MPLC (hexanes:EtOAc, 3:1) gave in order of elution: 23 mg (16%) of **6**, 6 mg (2%) of **8**, and 21 mg (10%) of **7** all as colorless oils. Spectral data (^{1}H NMR, IR, and MS) for **6** were in complete accord with literature values.[24] Additional spectra data for **6**. ^{13}C NMR (CDCl$_3$, 75 MHz): δ 206.5, 176.2, 51.8, 46.6, 34.6, 30.3, 17.0.

Spectral data for **7**. IR (neat): 2979, 1756, 1647, 1379, 1290, 1238, 1171, 1144, 1102, 1077, 1020, 954 cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 5.71 (bq, J = 1.3 Hz, C=CH, 1H), 3.65 (s, CO$_2$Me, 3H), 2.68 (bd, J = 12.1 Hz, MeCHC*H*$_a$H$_b$E), 2.35–2.16 (m, 2H), 1.97 (d, J = 1.5 Hz, *Me*C=CH, 3H), 1.39 (s, *Me*CR$_3$, 3H), 0.71 (d, J = 6.4 Hz, R$_2$CH*Me*, 3H); ^{13}C NMR (CDCl$_3$, 75 MHz): δ 173.3, 171.9, 116.8, 90.6, 51.8, 36.1, 35.1, 22.1, 14.1, 13.3 (quaternary carbon not observed). Anal. Calcd for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60. Found: C, 62.32; H, 7.87.

Spectral data for **8**. IR (CDCl$_3$): 2950, 1740, 1660, 1430, 1360, 1290, 1200, 1180, 1000 cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 3.67 (s, CO$_2$Me, 3H), 3.56 (s, CO$_2$Me, 3H), 3.09 (ddq, J = 5.1, 7.0, and 9.8 Hz; R$_2$C*H*Me, 1H), 2.88 (dd, J = 9.8 and 16.1 Hz, EC*H*$_a$H$_b$CH), 2.65 (dd, J = 3.1 and 15.2 Hz, EC*H*$_c$H$_d$CH, 1H), 2.51 (dd, J = 5.1 and 16.1 Hz, ECH$_a$*H*$_b$CH, 1H), 2.31 (ddq; J = 3.1, 6.6, and 9.2 Hz; R$_2$C*H*Me, 1H), 2.22 (dd, J = 9.2 and 15.2 Hz, ECH$_c$*H*$_d$CH, 1H), 1.94 (s, C=CMe, 3H), 1.37 (s, R$_3$C*Me*, 3H), 1.22 (d, J = 7.0, R$_2$CH*Me*, 3H), 0.64 (d, J = 6.6 Hz, R$_2$CH*Me*, 3H). ^{13}C NMR (CDCl$_3$, 75 MHz): δ 173.4, 172.9, 171.6, 129.0, 88.4, 52.8, 51.7, 38.0, 36.1, 35.3, 26.9, 22.2, 18.3, 13.8, 11.2 (quaternary carbon not observed). Anal. Calcd for $C_{16}H_{24}O_6$: C, 61.52; H, 7.74. Found: C, 61.75; H, 8.04.

2-Methyl-4-oxopentanoic Acid, Methyl Ester (9), and 3,5,β-Trimethyl-2(5*H*)furanone-5-propanoic Acid, Methyl Ester (10). Prepared by the general procedure A using 0.220 g (1.0 mmol) of chromium hexacarbonyl, 0.715 mL (1.05 mmol) of methyllithium, and 0.210 mL (2.1 mmol) of methyl methacrylate. Heating for 1 h, and purification of organics by MPLC (hexanes:EtOAc, 6:1) gave 59 mg (41%) of **9** and 17 mg (8%) of **10** as colorless oils. Spectral data for **9** were in complete accord with literature values.[25]

Spectral data for **10**. IR (neat): 2980, 1750, 1730, 1650, 1430, 1380, 1290, 1240, 1180, 1150, 1100, 1070, 1020 cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 6.87 (bq, J = 1.4 Hz, C=CH, 1H), 3.66 (s, CO$_2$Me, 3H), 2.43–2.37 (m, 1H), 1.89 (d, J = 1.4 Hz, C=CMe, 3H), 1.63–1.57 (m, 2H), 1.38 (s, R$_3$C*Me*, 3H), and 1.15 (d, J = 6.7 Hz, R$_2$CH*Me*, 3H). ^{13}C NMR (CDCl$_3$, 75 MHz): δ 170, 168, 152.1, 85, 52, 42.2, 35.3, 24.4, 18.9, 10.5 (quaternary carbon not observed). Anal. Calcd for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60. Found: C, 62.19; H, 7.32.

3-Phenyl-4-oxopentanoic Acid, Methyl Ester (11), 5-Methyl-4,α-diphenyl-2(5*H*)furanone-5-propanoic Acid, Methyl Ester (12), and 5-Methyl-4,α,α′-triphenyl-2(5*H*)-furanone-3,5-dipropanoic Acid, Dimethyl Ester (13). Prepared by the general procedure A using 0.220 g (1.0 mmol) of chromium hexacarbonyl, 0.75 mL (1.05 mmol) of methyllithium, and 0.178 g (1.1 mmol) of methyl cinnamate. Heating for 17 h and purification of organics by MPLC (hexanes:EtOAc, 6:1) afforded in order of elution: 48.6 mg (24%) of **11** as a colorless oil, 22 mg (4%) of **13** as a white solid, and 18 mg (5%) of **12** as a white solid.

Spectral data for **11** (^{1}H NMR and IR) were in complete accord with literature values.[26] Additional spectral data for **11**. ^{13}C NMR (CDCl$_3$, 75 MHz): δ 210, 172, 129.2, 128.3, 127.8, 54.9, 51.8, 36.6, 28.9 (substituted aryl carbon not observed).

Spectral data for **13**. IR (CDCl$_3$): 3065, 3031, 2997, 2954, 1754, 1601, 1494, 1438, 1375, 1286, 1253, 1174, 1127, 1032 cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.52–7.46 (m, ArH, 4H), 7.27–7.08 (m, ArH, 11H), 4.06 (dd, J = 4.7 and 11.2 Hz, EC*H*$_a$H$_b$CHR$_2$, 1H), 3.79–3.71 (m, 1H), 3.65 (s, CO$_2$Me, 3H), 3.48 (s, CO$_2$Me, 3H), 3.36 (dd, J = 4.8 and 9.6 Hz, R$_3$C*H*, 1H), 2.82–2.71 (m, 3H), 1.03 (s, R$_3$C*Me*, 3H). ^{13}C NMR (CDCl$_3$, 75 MHz): δ 172.6, 172.1, 166.3, 141.2, 138.3, 131.0, 129.6(2), 129.5(2), 129.0(2), 128.8(2), 128.4(2), 127.7(2), 127.6(2), 127.1(2), 89.9, 51.7(2), 46.8, 38.5, 36.6, 35.4, 23.4. Anal. Calcd for $C_{31}H_{30}O_6$: C, 74.60; H, 6.07. Found: C, 75.24; H, 6.20.

Spectral data for **12**. IR(CDCl$_3$): 3154, 3090, 3065, 3013, 2993, 2954, 2902, 1744, 1604, 1573, 1494, 1455, 1438, 1379, 1291, 1274, 1240, 1169, 1090 cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.63–7.18 (m, ArH, 10H), 6.33 (s, C=CH, 1H), 3.70 (dd, J = 3.8 and 10.9 Hz, EC*H*$_a$H$_b$CH, 1H), 3.32 (s, CO$_2$Me,

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[21] Korkowski, P. F.; Hoye, T. R.; Rydberg, D. B. *J. Am. Chem. Soc.* **1988**, *110*, 2676.

[22] Fischer, E. O.; Maasböl, A. *Chem. Ber.* **1967**, *100*, 2445.

[23] Cerfontain, H.; van Noort, R. C. M. *Synthesis* **1980**, 490.

[24] Atkins, R. C.; Trost, B. M. *J. Org. Chem.* **1972**, *37*, 3133.

[25] Beckwith, A. L.; O'Shea, D. M.; Westwood, S. W. *J. Am. Chem. Soc.* **1988**, *110*, 2565.

[26] Monte, W. T.; Bazier, M. M.; Little, R. D. *J. Org. Chem.* **1983**, *48*, 803.

3H), 2.75 (dd, *J* = 10.9 and 15.8 Hz, CH_2CH(Ph)C, 1H), 2.43 (dd, *J* = 3.8 and 15.8 Hz, ECH_aH_bCH, 1H), 1.41 (s, R_3CMe, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 171.5, 170.9, 138.0, 131.2, 131.0, 130.2, 129.9, 129.6, 129.4, 129.1, 128.8, 128.5, 127.7, 127.6, 127.5, 116.9, 90.9, 51.5, 48.1, 35.3, and 24.8. Anal. Calcd for $C_{21}H_{20}O_4$: C, 74.98; H, 5.99. Found: C, 74.96; H, 6.01.

4-Oxopentanoic Acid, 2-Propenyl Ester (15), and 2-(2-Oxopropyl)pentanoic Acid, Di-2-propenyl Ester (16). Prepared by the general procedure A using 1.64 g (7.5 mmol) of chromium hexacarbonyl, 5.4 mL (7.5 mmol) of methyllithium and 1.26 g (11.3 mmol) of allyl acrylate. Heating for 14 h, work-up, and MPLC (hexanes:EtOAc, 4:1) gave in order of elution **15** (14%) and **16** (1.248 g, 4.7 mmol, 62%) as colorless oils.

Spectral data for **15**: IR ($CDCl_3$) 2937, 1786, 1732, 1648, 1452, 1378, 1176, and 1095 cm^{-1}; ^{1}H NMR (300 MHz): δ 5.86 (ddt, *J* = 6.1, 10.3, and 17.1 Hz, $CH_2CH{=}CH_2$, 1H), 5.35 (ddt, *J* = 2.0, 2.7, and 17.1 Hz, $RCH{=}CH_cH_t$, 1H), 5.25 (ddt, *J* = 1.2, 2.0, and 10.3 Hz, $RCH{=}CH_cH_t$, 1H), 4.57 (ddt, *J* = 1.2, 2.0, and 6.1 Hz, $OCH_2CH{=}$, 2H), 2.76 (t, *J* = 6.4 Hz, C(O)-CH_2CHR_2, 2H), 2.63 (t, *J* = 6.4 Hz, C(O)CH_2CH_2E, 2H), 2.19 (s, C(O)Me, 3H). ^{13}C NMR (75 MHz): δ 208, 172, 132.0, 118.3, 65.5, 37.9, 29.9, 27.9.

Spectral data for **16**. IR ($CDCl_3$): 2950, 1730, 1640, 1440, 1440, 1370, 1250, 1190 cm^{-1}. ^{1}H NMR (300 MHz): δ 5.87 (ddt, *J* = 6.1, 10.3, and 17.1 Hz, $CH_2CH{=}CH_2$, 2H), 5.26 (br ddt, *J* = 2.7, 10.3, and 17.1 Hz, $RCH{=}CH_2$, 4H), 4.54–4.50 (5 line m, $OCH_2CH{=}$, 4H), 3.02 (m, R_3CH, 1H), 2.78 (dd, *J* = 9.6 and 14.8 Hz, C(O)$CH_aH_bCHR_2$, 1H), 2.41–2.30 (m, 3H), 2.25 (s, C(O)Me, 3H), 1.98 (dddd; *J* = 7.2, 7.2, 7.2, and 14.2 Hz; $R_2CHCH_cH_dCH_2R$, 1H), 1.76 (dddd; *J* = 7.2, 7.2, 7.2, and 14.4 Hz; $R_2CHCH_cH_dCH_2R$, 1H); ^{13}C NMR (75 MHz): δ 210, 172, 171, 132.0, 131.9, 118.6 (2), 65.5, 65.4, 46.8, 35.0, 31.2, 29.6, 16.0. Anal. Calcd for $C_{14}H_{20}O_5$: C, 62.67; H, 7.51. Found: C, 62.88; H, 7.89.

(*E*)-5-Ethenyl-2-hexenoic Acid, Dimethyl Ester (17). A slurry of chromium hexacarbonyl (1.01 g, 4.6 mmol, 0.7 M in dry THF) in a two-necked flask equipped with a reflux condenser was flushed with N_2 for 5 min. Methyllithium (3.3 mL, 4.6 mmol) was added via a syringe, and the resulting dark solution cooled to −78 °C. Methyl 4-bromocrotonate (1.1 mL, 9.4 mmol) was added via a syringe, and the reaction mixture was warmed to ambient temperature and stirred for 2 h. The crude reaction mixture was allowed to stand open to the air for ~1 h, passed through a plug of SiO_2 (EtOAc elution), and purified by MPLC (hexanes:EtOAc, 30:1) to give 739 mg (3.7 mmol, 81%) of **17** as a colorless oil. IR (neat): 2953, 1727(br), 1659, 1641, 1548, 1529, 1437, 1271, 1198, 1165, 1035 cm^{-1}; ^{1}H NMR (300 MHz): δ 6.83 (dt, *J* = 7.2 and 14.5 Hz, $RCH{=}CHE$, 1H), 5.85 (dt, *J* = 1.4 and 14.5 Hz, $RCH{=}CHE$, 1H), 5.80 (ddd; *J* = 7.6, 10.7, and 16.4 Hz, $RCH{=}CH_2$, 1H), 5.17 (dd, *J* = small and 10.7 Hz, $RCH{=}CH_cH_t$, 1H), 5.14 (dd, *J* = 0.9 and 16.4 Hz, $RCH{=}CH_cH_t$, 1H), 3.70 (s, CO_2Me, 3H), 3.67 (s, CO_2Me, 3H), 3.16 (q, *J* = 7.6 Hz, R_3CH, 1H), 2.62, (dddd; *J* = 1.4, 7.2, 7.6, and 14.7 Hz; $R_3CHCH_aH_b$, 1H), 2.48 (dddd, *J* = 1.4, 7.2, 7.6, and 14.7 Hz; $R_3CHCH_aH_b$, 1H); ^{13}C NMR (75 MHz): δ 174, 167, 145.1, 134.5, 123.1, 116.3, 52.1, 51.5, 48.7, 34.2. Anal. Calcd for $C_{10}H_{14}O_4$: C, 60.59; H, 7.12. Found: C, 60.43; H, 7.18.

4,5,β-Trimethyl-2(5*H*)furanone-5-propanoic Acid, Methyl Ester (18). Competition Experiment. Using the general procedure A, 2.12 g (9.6 mmol) of chromium hexacarbonyl, 6.7 mL (9.6 mmol) of methyllithium, 2.6 mL (24.5 mmol) of methyl crotonate, and 2.6 mL (24.3 mmol) of methyl methacrylate was heated for 16 h. Workup and MPLC (hexanes:EtOAc, 6:1) afforded **6** (11%), **7** (8%), **8** (19%), **9** (5%), **10** (16%), and 245 mg (1.2 mmol, 13%) of **18** as colorless oils.

Spectral data for **18**. IR (neat): 2979, 2952, 1752, 1645, 1458, 1436, 1213, 1168, 989, 945 cm^{-1}. ^{1}H NMR (300 MHz): δ 5.59 (bq, *J* = 1.4 Hz, C=CH, 1H), 3.50 (s, CO_2Me, 3H), 2.31 (ddq, *J* = 3.6, 7.0, and 8.6 Hz, $ECHMeCH_2R$, 1H), 2.16 (dd, *J* = 8.5 and 14.4 Hz, $R_2CHCH_aH_bCR_3$, 1H), 1.88 (d, *J* = 1.6 Hz, $MeC{=}CHR$, 3H), 1.73 (dd, *J* = 3.6 and 14.4 Hz, $R_2CHCH_aH_bCR_3$, 1H), 1.33 (s, R_3CMe, 3H), 1.06 (d, *J* = 7.0 Hz, $ECH(Me)CH_2R$, 3H). ^{13}C NMR (75 MHz): δ 176.4, 171.2, 116.9, 88.5, 60.3, 51.7, 40.3, 34.5, 24.3, 19.1, 13.1. Anal. Calcd for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60. Found: C, 61.98; H, 7.86.

General Procedure B: Reaction of Tetramethylammonium Pentacarbonyl(1-oxidoethylidene)chromate(0) (22) with Electron Deficient Alkenes under Thermal Conditions. To a solution of tetramethylammonium pentacarbonyl(1-oxidoethylidene)chromate(0) (**22**) in THF in an airless flask equipped with a reflux condenser was flushed with N_2 for 5 min. The α,β-unsaturated carbonyl compound was added via syringe, and the reaction mixture was heated at 75 °C (external bath temperature). The crude brown-green reaction mixture was filtered through a Celite pad (0.5 cm) and the pad was washed with THF. The solvent was removed on a rotary evaporator at water aspirator pressure and the residue was dissolved in hexanes−EtOAc (1:1). Air oxidation in the sunlight gave a clear solution with some green precipitate. The solution was filtered through a Celite pad (0.5 cm) and the pad was washed with hexanes−EtOAc (1:1). Removal of the solvent (rotary evaporator) affords in most cases pure product.

4-Oxopentanoic Acid, Methyl Ester (2). Prepared by the general procedure B using 618 mg (2.00 mmol) of **22** and 956 μL (2.20 mmol) of methyl acrylate. Heating for 24 h, air oxidation (sunlight) for 90 min, and workup afforded 206 mg (1.58 mmol, 79%) of **2** as a colorless oil. Spectral data were in complete accord with literature values.[23]

2-Methyl-4-oxopentanoic Acid, Methyl Ester (6), and 4,5,α-Trimethyl-2(5*H*)furanone-5-propanoic Acid, Methyl Ester (7). Prepared by the general procedure B using 618 mg (2.00 mmol, 0.1 M in THF) of **22** and 956 μL (2.20 mmol) of methyl crotonate. Heating for 24 h, air oxidation (sunlight), and Celite filtration afforded 188 mg of crude product. The crude mixture was purified by short-path distillation to give 152 mg of a mixture of **6** and **7** (40 and 8% yield, respectively, by ^{1}H NMR) as a colorless oil.

3-Phenyl-4-oxopentanoic Acid, Methyl Ester (11), and 5-Methyl-4-phenyl-2(5*H*)-furanone (23). Prepared by the general procedure B using 680 mg (2.2 mmol, 0.1 M in THF) of **22** and 324 mg (2.00 mmol) of methyl cinnamate. Heating for 24 h, air oxidation (sunlight, 4 h), Celite filtration, and MPLC (hexanes−EtOAc, 4:1) afforded in order of elution: 43 mg (0.27 mmol, 13%) of methyl cinnamate, 54 mg (0.26 mmol, 13%) of **11**, and 54 mg (0.31 mmol, 16%) of **23** all as colorless oils. Spectral data of **23** were in complete accord with literature values.[27]

Triester 21. Prepared by the general procedure B using 0.66 g (2.1 mmol, 0.7 M in THF) of **22** and 0.85 g (3.2 mmol) of triester **20**. Heating for 4 h, workup, and MPLC (hexanes−EtOAc, 9:1) afforded 0.41 g (1.3 mmol, 63%) of **21**. IR ($CDCl_3$): 2950, 1730, 1435, 1350, 1220, 1200, 1190 cm^{-1}; ^{1}H NMR (300 MHz): δ 3.73 (s, CO_2Me, 3H), 3.72 (s, CO_2Me, 3H), 3.65 (s, CO_2Me, 3H), 3.06 (m, CHR_3, 1H), 2.86 (d, *J* = 2.7 Hz, $HCCCH_2R$, 2H), 2.67 (dd, *J* = 8.3 and 16.4 Hz, ECH_aH_bCH, 1H), 2.53 (dd, *J* = 6.5 and 14.9 Hz, $R_3CCH_cH_dCH$, 1H), 2.33 (dd, *J* = 5.5 and 16.4 Hz, ECH_aH_bCH, 1H), 2.24 (s, C(O)Me, 3H), 2.16 (s, *H*CCR, 1H), 2.02 (dd, *J* = 5.5 and 14.9 Hz, $R_3CCH_cH_dCH$, 1H); ^{13}C NMR (75 MHz): δ 210, 171.9 (2), 170.3, 72.2, 55, 52.9, 51.9, 43.8, 36.6, 32.8, 28, and 23.6. Anal. Calcd for $C_{15}H_{20}O_7$: C, 57.69; H, 6.45. Found: C, 57.47; H, 6.43.

General Procedure C: Reaction of Tetramethylammonium Pentacarbonyl(1-oxidoethylidene)chromate(0) (22) with Electron Deficient Alkenes under Photochemical Conditions. Through a solution of tetramethylammonium pentacarbonyl(1-oxidoethylidene)chromate(0) (**22**) in THF (0.1 M) in a threaded pressure tube was bubbled N_2 for 5 min. The α,β-unsaturated carbonyl compound was added

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(27) a) Scharf, H.-D.; Wolters, E. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 682. b) Sharf, H.-D.; Wolters, E. *Chem. Ber.* **1978**, *111*, 639.

via syringe, the reaction vessel was capped with a teflon screw cap, and the mixture was irradiated (450 W Conrad-Hanovia 7825 medium-pressure mercury lamp, Pyrex well) for 21–36 h. The crude brown-green reaction mixture was filtered through a Celite pad (0.5 cm) and the pad was washed with THF. The solvent was removed on a rotary evaporator at water aspirator pressure and the residue was dissolved in hexanes–EtOAc (1:1). Air oxidation in the sunlight or by irradiation as above, to remove any complex bound chromium, gave a clear solution with a green-brown precipitate. The solution was filtered through a Celite pad (0.5 cm), the pad was washed with hexanes–EtOAc (1:1), and the solvents were removed (rotary evaporator) to afford, in most cases, pure product. Analytical samples were prepared by short-path distillation or MPLC.

3-Methyl-4-oxopentanoic Acid, Methyl Ester (6), and 2-Ethylidene-3-methyl Pentanoic Acid, Dimethyl Ester (24). Prepared by the general procedure C using 620 mg (2.01 mmol) of **22** and 424 μL (4.00 mmol) of methyl crotonate. Irradiation for 20 h followed by air oxidation (sunlight, 2.5 h) followed by MPLC (hexanes–EtOAc, 3:1) afforded in order of elution: 144 mg (0.73 mmol, 36%) of **24** and 181 mg (1.26 mmol, 63%) of **6** both as a colorless oils. **24** is a ca. 5:1 mixture of double bond isomers. ^{1}H NMR, IR, and GLC-MS data for **24** were in complete accord with literature values.[28] Additional spectral data for **24**. ^{13}C NMR (22.5 MHz, major isomer): δ 173.2 (CO, s), 167.3 (CO, s), 138.0 (*C*H=C, d), 135.5 (C2, s), 51.2 (OMe, q), 51.1 (OMe, q), 39.2 (C4, t), 28.9 (C3, d), 18.9 (Me, q), 13.9 (Me, q).

A similar reaction of 309 mg (1.00 mmol) of **22** with 212 μL (2.00 mmol) of methyl crotonate, but under 6 atm of CO, gave after irradiation for 48 h and air oxidation a white precipitate containing $Cr(CO)_6$ and **6**. The mixture was triturated with a few milliliters of absolute EtOH and filtered through a short SiO_2 column to remove $Cr(CO)_6$. After solvent removal (rotary evaporator), 82 mg (0.57 mmol, 57%) of **6** was isolated as a colorless oil.

2,4-Hexanedione (25). Prepared by the general procedure C using 618 mg (2.00 mmol) of **22** and 175 μL (2.10 mmol) of 3-buten-2-one. Irradiation for 36 h followed by air oxidation (sunlight, 45 min) gave after filtration 171 mg (1.50 mmol, 75%) of **25** as a colorless oil. No further purification was necessary. Spectral data for **25** were in complete accord with commercially available sample (Aldrich Chem. Co.).

3-(1-Oxoethyl)-1-cyclopentanone (26). Prepared by the general procedure C using 620 mg (2.01 mmol) of **22** and 176 μL (2.10 mmol) of 2-cyclopenten-1-one. Irradiation for 36 h followed by air oxidation (sunlight, 45 min) followed by MPLC (hexanes–EtOAc, 4:1) afforded 242 mg (1.92 mmol, 96%) of **26** as a colorless oil. ^{1}H NMR, IR, and GLC-MS data of **26** were in complete accord with literature values.[26] Additional spectral data for **26**. ^{13}C NMR (22.5 MHz): δ 216.4 (C1, s), 208.2 (CO, s), 48.2 (C3, d), 39.6 (t), 37.3 (t), 28.4 (Me, q), 25.6 (C4, t).

3-(1-Oxoethyl)-1-cyclohexanone (27) and 2-(3-Oxocyclohexyl)-2-cyclohexen-1-one (28). Prepared by the general procedure C using 618 mg (2.00 mmol) of **22** and 212 μL (2.00 mmol) of 2-cyclohexen-1-one. Irradiation for 23 h and air oxidation (sunlight, 4 h) followed by short-path distillation afforded 194 mg of a an unseparable (MPLC) mixture of **27** (16%) and **28** (45%) as a colorless oil. The yields were determined by ^{1}H NMR and GLC. Analytical samples were obtained by HPLC (hexanes–EtOAc, 6:1). ^{1}H NMR and IR data for **27**[29] and **28**[30] were in complete accord with literature values. Additional spectral data for **27**. ^{13}C NMR: (22.5 MHz) δ 209.7, 208.3, 50.8, 42.4, 40.8, 28.2, 27.1, 24.9; GLC-MS (*m/z*) 98 ($M^+ - CH_2{=}CO$). Additional spectral data for **28**. ^{13}C NMR (22.5 MHz): δ 211.1, 198.3, 144.2, 141.8, 46.4, 41.3, 38.8, 37.7, 30.6, 26.1, 25.0, 22.8; GLC-MS (*m/z*) 192 (M^+).

4-Oxopentanoic Acid, Methyl Ester (2). Prepared by the general procedure C using 618 mg (2.00 mmol) of **22** and 198 μL (2.20 mmol) of methyl acrylate. Irradiation for 21 h and air oxidation (sunlight, 4 h) followed by short-path distillation afforded 90 mg (0.76 mmol, 38%) of **2** as a colorless oil.

4-Cyano-2-butanone (29). Prepared by the general procedure C using 618 mg (2.00 mmol) of **22** and 145 μL (2.20 mmol) of acrylonitrile. Irradiation for 21 h and air oxidation (sunlight, 4 h) followed by short-path distillation afforded 90 mg (0.76 mmol, 38%) of **29** as a colorless oil. ^{1}H NMR and IR data of **29** were in complete accord with literature values.[31] Additional spectral data for **29**: ^{13}C NMR (22.5 MHz) δ 203.6 (C2), 188.9 (CN), 38.6 (C3), 29.5 (C4), 11.32 (C4).

4-Phenyl-2-butanone (30). Prepared by the general procedure C using 618 mg (2.00 mmol) of **22** and 252 μL (2.20 mmol) of styrene. Irradiation for 24 h and air oxidation (sunlight, 6 h) followed by MPLC (hexanes–EtOAc, 4:1) gave 18 mg (0.12 mmol, 6%) of **30** as a colorless oil. Spectral data of **30** were in complete accord with a commercially available sample (Aldrich Chem. Co.).

2-Deuterio-3-methyl-4-oxopentanoic Acid, Methyl Ester (31), and 3-Deuterio-3-methyl-4-oxopentanoic Acid, Methyl Ester (32). Prepared by the general procedure C using 623 mg (2.02 mmol) of **22**, 233 μL (2.20 mmol) of methyl crotonate, and 181 μL (10.0 mmol) of D_2O. Irradiation for 24 h and air oxidation (sunlight, 4 h) followed by filtration gave 173 mg (1.20 mmol, 59%) of **31**[32] and **32** as an inseparable 1:1 mixture.[33] Spectral data for **31** and **32** from a 1:1 isomer mixture. IR (film): 2960, 2880, 1730, 1700, 1430, 1200 cm^{-1}; ^{1}H NMR (90 MHz): δ 3.66 (s, OMe), 3.08–2.63 (m, 1.5 H), 2.28 (m, 0.5 H), 2.22 (s H5, 3H), 1.56 (d, J = 6.9 Hz, MeC3, 3H). ^{13}C NMR (22.5 MHz): δ 210.5 (C4), 172.6 (C1), 51.5 (OMe), 42.5 (C5), 36.5 (C3), 36.2 (t, C3, **32**), 28.2 (C2), 27.9 (t, C2, **31**), 27.6 (t, C2, **31**), 16.3 (MeC3). GLC-HRMS (EI) exact mass calcd for $C_7H_{11}DO_3$ *m/z* 145.0849, obs 145.0851.

Acknowledgment. Financial support for this work was obtained from the donors of the Petroleum Research Fund administered by the American Chemical Society and by Grant GM-38854 awarded by the DHHS. The University of Minnesota Graduate School is acknowledged for providing a Dissertation Fellowship (to J.A.S.) in 1992–93.

OM940473C

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[28] For spectral data and some recent syntheses of **23**, see: a) Fissekis, J. D.; Sweet, F. *J. Org. Chem.* **1973**, *38*, 1963. b) Ikeda, M.; Hirano, T.; Tsuruta, T. *Tetrahedron* **1975**, *30*, 2217. c) See ref. 22.

[29] For some recent syntheses of **27**, see: a) Ref. 5a. b) Scheffold, R.; Orlinski, R. *J. Am. Chem. Soc.* **1983**, *105*, 7200.

[30] For spectral data and syntheses of **28**, see: a) Leonard, N. J.; Musliner, W. J. *J. Org. Chem.* **1966**, *31*, 639. b) White, D. A.; Baizer, M. M. *J. Chem. Soc., Perkin I* **1973**, 223. c) Chui, C.; Corriu, R. J. P.; Reye, C. *Synthesis* **1983**, 294. d) Jasizak, J. *Tetrahedron* **1987**, *28*, 4323.

[31] For some recent syntheses of **29**; see: a) Stetter, H.; Kuhlmann, H. *Chem. Ber.* **1976**, *109*, 2890. b) Ref. 27b.

[32] Ester **31** is a mixture of diastereomers as evidenced by ^{13}C NMR spectroscopy.

[33] Minor amounts of polydeuterated products were detected as well.