Articles

Photolytic Reaction of Hydroxy Fischer Carbene Complexes: Synthesis of α-Hydroxy Esters

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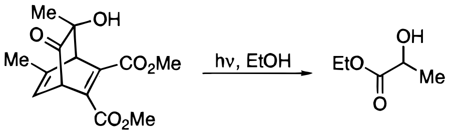
Photolytic reaction of *in situ* generated pentacarbonyl(1-hydroxyalkylidene)chromium complexes in the presence of an alcohol, under 6 atm of carbon monoxide, affords α-hydroxy-substituted esters in low to moderate yield. Acetals, formed *via* thermal decomposition of the carbenes, are in some cases the major product.

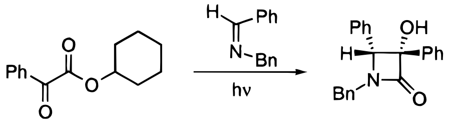
Introduction

Photolytic reactions of Fischer chromium carbene complexes, chemistry mainly developed by Hegedus and co-workers, have recently found extensive use in organic synthesis producing ketene-derived products.[1] For example, Fischer chromium carbene complexes have been used to prepare cyclobutanones,[2] *β*-lactones,[3] *γ*-lactones,[4] lactames,[2b,5] azapenams,[6] bis-azapenams,[7] amino acids, allenes,[8] peptides,[9] bicyclo[4.2.1]nonanone derivatives,[10] 2-butene-1,4-diones,[11] diazabicycloctanone derivatives,[12] and polycyclic aromatic compounds.[13] These reactions are thought to proceed *via* an intermediately formed ketene, probably metal bound, followed by addition of a nucleophilic or cycloaddition to an unsaturated compound. The reaction conditions are mild, and the regio- and stereochemistries observed from photolytic reactions of Fischer carbenes parallel those of free ketenes generated by more conventional methods such as acid halides and a base. α-Hydroxy ketenes cannot, for obvious reasons, be generated from acid halides, and only a few isolated cases of ketene intermediates of this type have been reported in the literature. To our knowledge, only methyl and phenyl substituted α-hydroxy ketenes have been generated in the presence of water,[14] alcohols,[15] or imines[16] to form α-hydroxy carboxylic acids, α-hydroxy esters, and *β*-lactams, respectively. Two representative examples thereof are depicted in Schemes 1 and 2.

Scheme 1



Scheme 2



As part of an ongoing effort in our laboratories to develop synthetically useful reactions employing Fischer carbene complexes, we envisioned a mild and more general method for the generation of α-hydroxy ketenes from pentacarbonyl(1-hydroxyalkylidene)metal complexes. Pentacarbonyl(1-hydroxyalkylidene)metal complexes are rarely investigated compounds, and only a few scattered reports can be found in the literature. For example, pentacarbonyl(1-hydroxyethylidene)- and pentacarbonyl(1-hydroxy-1-phenylmethylene)carbene complexes are known for all group 6 metals.[17] In addition, pentacarbonyl(1-hydroxy-1-(2-thienyl)methylene)chro-

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[⊗] Abstract published in *Advance ACS Abstracts*, October 15, 1996.

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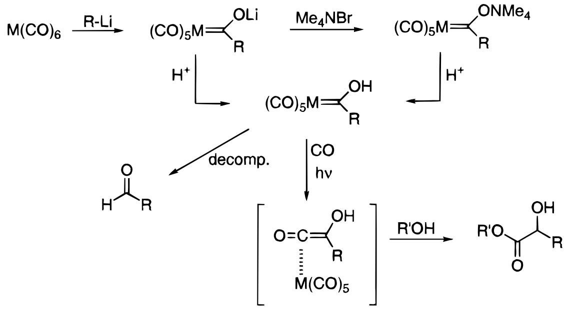
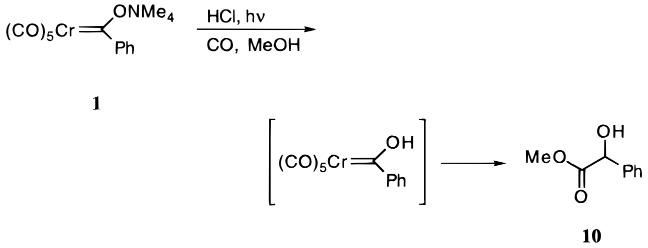
Scheme 3



Scheme 4



mium[18] and tungsten[19] and pentacarbonyl(1-hydroxy-1-cyclopropylmethylene)chromium[20] have been isolated.[17a,21] These complexes are readily prepared by addition of an acid, such as HBr, HCl, H_2SO_4, or HBF_4, to the corresponding lithium or tetramethylammonium pentacarbonyl(1-oxoalkyl)metalate(1−)[22] salts formed by addition of the appropriate alkyllithium to chromium, molybdenum, or tungsten hexacarbonyl followed by, for the tetramethylammonium salt, exchange of the counterion (Scheme 3). Isolated 1-hydroxy-substituted carbenes are thermally unstable and decompose rapidly at ambient temperature to the corresponding aldehyde.[23] For example, pentacarbonyl(1-hydroxy-1-phenylmethylene)chromium decomposes to benzaldehyde upon standing at room temperature (R = Ph in Scheme 3).[17g,24] Thus, in order to form ketene-derived products, the rates of the formation and subsequent reaction of the ketene intermediate must be faster in comparison to the rate of the thermal decomposition. Herein is reported the scope and limitations of the formation of α-hydroxy-substituted esters[25] *via* nucleophilic addition of alcohols to ketene intermediates generated by photolysis of 1-hydroxy-substituted Fischer carbene complexes.

Results and Discussion

In our initial experiment, addition of HCl (37% aqueous) to a pressure tube containing a solution of tetramethylammonium benzoylpentacarbonylchromate(1−) (**1**) in methanol gave the hydroxy carbene, as apparent by the immediate color change from yellow to deep red (Scheme 4). The pressure tube was charged with CO (4 atm), and the solution was irradiated (450 W, Conrad-Hanovia medium-pressure mercury lamp, Pyrex well) at ambient temperature for 20 h, producing the α-hydroxy ester **10** in a low isolated yield (12%, entry 1, Table 1). A similar result (13%) was obtained using HCl in Et_2O (1 M) in place of aqueous HCl. Although the yield of hydroxy ester was doubled by employing a higher CO pressure (6 atm, 24%, entry 3), an even more substantial increase was realized by a combination of lower initial reaction temperature (−50 °C) and higher CO pressure (6 atm), affording **10** in 60% yield (entry 4).

The major byproduct in all of the above reactions, especially those performed at ambient temperature, was [dimethoxymethyl]benzene (benzaldehyde dimethyl acetal), deduced from ^{1}H NMR of the crude reaction mixtures. Since all resonances were broad and unresolved due to residual chromium species, the amount of acetal formed in each reaction was hard to quantify by ^{1}H NMR. In the experiments performed at ambient temperature, the ratio of acetal to ester was roughly estimated to be 3−5:1 from these spectra. (Note that little or no benzaldehyde was observed.) The acetal was, in the case of complex **1**, completely lost during workup.

Next, we examined the photochemical reaction of a number of *in situ* generated hydroxy-substituted chromium and tungsten Fischer carbenes under the optimal conditions discussed above (HCl−Et_2O, 1 M, −50 °C) and the results thereof are summarized in Table 1. For reactions using methanol as the solvent, the yield of α-hydroxy esters ranged from 10% to 62% and was in most cases accompanied by the formation of a substantial amount of acetal. A modest diastereoselectivity was observed when the isobutyl-substituted complex **4** (entry 11) was employed, and a 4.1:1 ratio of *SS*/*RR*:*SR*/*RS* was isolated. Acetals in various amount are most likely formed in all of the reactions shown in Table 1, and the absence of an acetal for a given reaction probably only reflects the acetal's instability to the workup conditions. For example, ^{1}H NMR spectra of the crude reaction mixture obtained from reaction of complex **5** with methanol showed a 2:1 ratio of acetal to α-hydroxyester, a ratio that was reduced to about 1:1 after chromatography (entry 12). Substituting ethanol for methanol as the solvent (and the nucleophile) resulted in a significant drop in yield, and the ester **11** and the acetal **12** were isolated in 19% and 7% yields, respectively (entry 5). We presently have no explanation for the decrease in yield in this case.

Employing the nucleophile as solvent (methanol, ethanol) proved to give better yields of α-hydroxy esters compared to reactions performed in an inert solvent (diethyl ether) using an added nucleophile (benzenemethanol). In all cases using benzenemethanol, no or only a minute amount of the ester was isolated. Thus, both the 1-oxopentyl and the cyclopropylcarbonyl complexes, **3** and **6** gave the corresponding α-hydroxy esters

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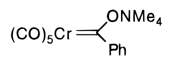
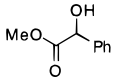
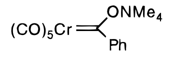
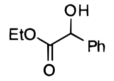
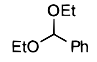
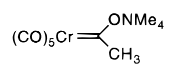
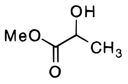
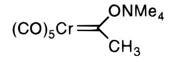
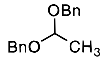
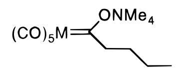
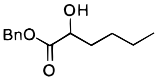
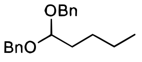
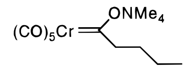
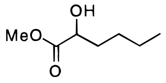
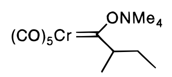
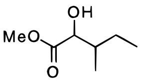
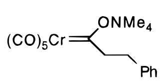
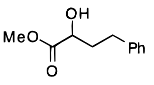
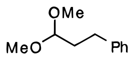
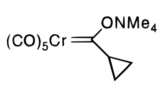
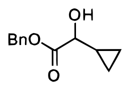
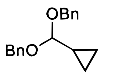
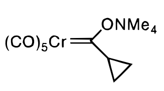
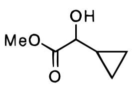
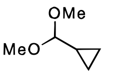
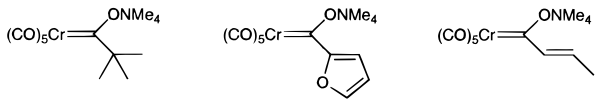
(25) For some recent syntheses of α-hydroxy acid esters, see: (a) Julia, M.; Pfeuty-Saint James, V.; Ple, K.; Verpeaux, J.-N.; Hollingworth, G. *Bull. Soc. Chim. Fr.* **1996**, *133*, 15. (b) Satoh, T.; Onda, K.-I.; Yamakawa, K. *J. Org. Chem.* **1991**, *56*, 4129. C) Orito, K.; Seki, Y.; Suginome, H.; Iwadare, T. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 2013.

Table 1. Photochemical Reaction of Hydroxy Fischer Carbenes

Entry	Complex[a,b]	Alcohol	Products (Yield%)	
		MeOH		
1	1		**10** (12)[d]	
2	1		**10** (13)[d]	
3	1		**10** (24)[e]	
4	1		**10** (60)	
		EtOH		
5	1		**11** (19)	**12** (7)
		MeOH		
6	2		**13** (10)	
		BnOH		
7	2		**14** (30)	
		BnOH		
8	3		**15** (21)	**16** (14)[f]
9	3[g]		**15** (2)	**16** (27)[f]
		MeOH		
10	3		**17** (62)[h]	
		MeOH		
11	4		**18** (28)[i]	
		MeOH		
12	5		**19** (22)	**20** (27)
		BnOH		
13	6		**21** (4)	**22** (20)[f]
		MeOH		
14	7		**23** (19)	**24** (8)

[a] The hydroxy carbene was formed *in situ* by addition of HCl (Et_2O, 1 M, 5 equiv) to the corresponding tetramethylammonium pentacarbonyl(1-oxoalkyl)-chromate(1−) salt shown. [b] The formed solution of the hydroxy carbene (ca. 0.04 M) was irradiated for 20−24 h under 6 atm of CO at an initial temperature of −50 °C, unless otherwise stated. For details see the Experimental Section. [c] Isolated yields after chromatography. [d] Reaction performed at room temperature using HCl(aq) at 4 atm of CO. [e] Reaction performed at ambient temperature at 6 atm of CO. [f] The acetal was always accompanied by a small amount of impurity. [g] Small amounts of the acetal were isolated together with $W(CO)_6$. [h] Minor amounts (<5%) of the dimethyl acetal were observed after chromatography. [i] A 4.1:1 mixture of *SS/RR:SR/RS* was isolated.



7 **8** **9**

Figure 1.

15 and **21** and the acetals **16** and **22**[26] when reacted with benzenemethanol (entries 8 and 13). The yields of the esters **15** and **21** were very low, and the structure of the latter product was only tentatively assigned. Increasing the concentration of the 1-oxopentyl complex **3** from 0.04 to 0.14 M resulted in a higher yield of the acetal **16** at the expense of ester **15** (entry 9). No benzyl ester was isolated from photolysis of the acetyl complex **2** in the presence of benzenemethanol (entry 7).

In an attempt to minimize acetal formation, we turned to the closely related Fischer tungsten carbenes which, compared to their chromium counterparts, usually have a somewhat higher thermal stability. With this fact in mind, we examined the reaction of the tungsten analogs of complex **2** and **3**, with both methanol and benzenemethanol as nucleophile. Somewhat to our disappointment, small amounts of a myriad of unidentified products were obtained from reaction of **2-W** with methanol. In addition, but still uninteresting, the tungsten analogs of **2** and **3** gave acetals in very low yield when reacted with benzenemethanol.

In addition to the alcohols, a few other nucleophiles were briefly examined. Photolytic reaction of **1** in a THF−H_2O (9:1) mixture did not produce any of the expected α-hydroxy acid, and not surprisingly, reaction of **1** with amines (diethylamine and benzylamine) did not afford an α-hydroxy amide. The latter result is most likely due to the facile deprotonation of the hydroxy group prior to ketene formation.[27] In a related study, α-hydroxy amides were obtained in fair to good yield from reaction of pentacarbonyl(1-(trimethylsiloxy)alkylidene)chromium complexes with 4-methoxybenzenamine under photochemical conditions.[28] α-Hydroxy esters could not be prepared using siloxy-substituted carbenes, due to the facile cleavage of the silicon−oxygen bond by alcohols. Some additional chromium salts were examined, and although the carbenes were completely consumed, no ester or acetal formation was observed when tetramethylammonium pentacarbonyl(2,2-dimethyl-1-oxopropyl)chromate(1−) (**7**),[29] tetramethylammonium pentacarbonyl(2-furylcarbonyl)chromate(1−) (**8**),[30] or tetramethylammonium pentacarbonyl(1-oxo-2-butenyl)chromate(1−) (**9**)[31] was reacted with HCl and methanol. See Figure 1. Although the intermediately formed hydroxy carbenes were not isolated, upon addition of HCl, the color changed as would be expected for the formation of the carbenes.

In conclusion, we have developed a method for the preparation of α-hydroxy methyl and ethyl esters in low to moderate yield. Although the yield is moderate at

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(26) Due to their instability on silica gel, upon isolation of the acetals a small amount impurity was always obtained. Correct elemental analyses could not be obtained from **16** and **22**.

(27) The deep red color of the hydroxy carbene solution immediately changed to yellow, the color of the tetramethylammonium salt, upon addition of the amine.

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best, this method represents a short entry to α-hydroxy esters. It is conceivable that the yields can be substantially improved upon irradiation of the reaction mixture at a low temperature (−50 °C) for an extended period of time or irradiated at higher CO pressure. Both variations are at present unavailable to us.

Experimental Section

Methanol was distilled from CaH_2 prior to use. All other chemicals were prepared according to referenced literature procedures or used as received from commercial sources. All manipulations were performed under an atmosphere of argon or carbon monoxide. Solvents were removed from crude reaction mixtures and purified compounds using a rotary evaporator at water aspirator pressure unless otherwise stated.

All NMR spectra were determined in $CDCl_3$ at 270 MHz (^1H 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, ^1H and ^{13}C) or $CDCl_3$ (77.00, ^{13}C) internal standards. 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. $^1H-^1H$ coupling constants are reported as calculated from spectra; thus, a slight difference between $J_{a,b}$ and $J_{b,a}$ is usually obtained.

Methyl 2-Hydroxy-2-phenylacetate (10). To a −50 °C cold slurry of tetramethylammonium benzoylpentacarbonylchromate(1−)[17g] (**1**) (371 mg, 1.00 mmol) in methanol (20 mL) in an ACE-Glass pressure tube was added HCl (5.0 mL, 5.00 mmol, 1 M in Et_2O) under an argon atmosphere. A red solution was immediately formed. The tube was capped with a pressure head, pressurized to 6 atm of CO, and immersed in an Erlenmeyer flask containing a −50 °C cold solution of CO_2−acetone. The flask was irradiated (450 W Conrad-Hanovia 7825 medium-pressure mercury lamp, Pyrex well) overnight (20 h) allowing the temperature of the Erlenmeyer flask to reach ambient temperature slowly. The resulting yellow solution, containing a substantial amount of chromium hexacarbonyl, was removed by pipet, and the tube was rinsed with a few portions of hexanes (a total of 10 mL). H_2O (15 mL) was added to the methanol−hexane mixture followed by extraction with dichloromethane (3 × 20 mL). The combined organic phases were dried ($MgSO_4$) and filtered, and the solvents were removed to give a yellow oil together with some crystalline $Cr(CO)_6$. The crude product was purified by column chromatography using hexanes−EtOAc (3:7) as eluent, affording **10** (100 mg, 0.60 mmol, 60%) as faint yellow crystals. Spectroscopic data were in complete accordance with literature values.[32]

Ethyl 2-Hydroxy-2-phenylacetate (11) and [Diethoxymethyl]benzene (12). A solution of tetramethylammonium benzoylpentacarbonylchromate(1−) (**1**) (371 mg, 1.00 mmol) in ethanol (20 mL) was reacted with HCl (5.0 mL, 5.00 mmol, 1 M in Et_2O) and CO as described above. Irradiation (20 h), extraction, and chromatography using hexanes−EtOAc (1:1) followed by hexanes−EtOAc (3:7) gave, in order of elution, **12** (12 mg, 0.07 mmol, 7%) and **11** (34 mg, 0.19 mmol, 19%) as a colorless oil and faint yellow crystals, respectively. Spectroscopic data of **11**[33] and **12**[34] were in complete accordance with literature values.

Methyl 2-Hydroxyacetate (13). A solution of tetramethylammonium acetylpentacarbonylchromate(1−)[17g] (**2**) (309 mg, 1.00 mmol) and benzenemethanol (2.10 mL, 20.0 mmol) in Et_2O (20 mL) was reacted with HCl (5.0 mL, 5.00 mmol, 1 M in Et_2O) and CO as described above. Irradiation (20 h), extraction, and chromatography using pentane−Et_2O (8:2), followed by pentane−Et_2O (7:3) and pentane−Et_2O (1:1), gave **13** (10 mg, 0.10 mmol, 10%) as a colorless oil. Spectroscopic data of **13** were in complete accordance with literature values.[35]

1,1′-[Ethylidenebis(oxymethylene)]bis(benzene) (14). A solution of tetramethylammonium acetylpentacarbonylchromate(1−) (**2**) (309 mg, 1.00 mmol) and benzenemethanol (2.10mL, 20.0 mmol) in Et_2O (20 mL) was reacted with HCl (5.0 mL, 5.00 mmol, 1 M in Et_2O) and CO as described above. Irradiation (20 h) produced a pink suspension[36] that was purified by extraction and chromatography, using hexanes−EtOAc (1:1), followed by hexanes−EtOAc (3:7), to give **14** (72 mg, 0.30 mmol, 30%) as a faint yellow oil. Spectroscopic data of **14** were in complete accordance with literature values.[37]

A similar reaction of solution of tetramethylammonium acetylpentacarbonyltungstate(1−)[17g] (**2-W**) (441 mg, 1.00 mmol) and benzenemethanol (0.52 mL, 5,00 mmol) in Et_2O (20 mL) with HCl (5.0 mL, 5.00 mmol, 1 M in Et_2O) and CO as described above gave, after irradiation (20 h), extraction, and chromatography using, in sequence, pentane−Et_2O (8:2), pentane−Et_2O (7:3), and pentane−Et_2O (1:1), a small amount of **14** together with $W(CO)_6$.

Benzyl 2-Hydroxyhexanoate (15) and 1,1′-[Pentylidenebis(oxymethylene)]bis(benzene) (16). A solution of tetramethylammonium pentacarbonyl(1-oxopentyl)chromate(1−)[38] (**3**) (351 mg, 1.00 mmol) and benzenemethanol (0.21 mL, 2.00 mmol) in Et_2O (20 mL) was reacted with HCl (5.0 mL, 5.00 mmol, 1 M in Et_2O) and CO as described above. Irradiation (20 h), extraction, and chromatography using, in sequence, hexanes−EtOAc (1:1) and hexanes−EtOAc (3:7) gave, in order of elution, **16** (59 mg, 0.21 mmol, 21%) and **15** (30 mg, 0.14 mmol, 14%) as colorless liquids. Spectroscopic data of **15** were in complete accordance with literature values.[39] Spectroscopic data for **16**: ^1H NMR δ 7.37−7.32 (m, 10H), 4.76 (t, $J = 5.9$ Hz, 1H), 4.68 (d, $J = 12.1$ Hz, 2H), 4.58 (d, $J = 11.7$ Hz, 2H), 1.78 (m, 2H), 1.45−1.27 (m, 4H), 0.91 (t, $J = 6.9$ Hz, 3H); ^{13}C NMR δ 138.2 (+), 128.2 (−), 127.6 (−), 127.4 (−), 102.1 (−), 66.9 (+), 32.9 (+), 26.8 (+), 22.4 (+), 13.8 (−); IR (film) 3031, 2956, 2938, 2870, 1454, 1127, 1108, 1042, 1025, 734, 697 cm^{-1}.

A similar reaction of tetramethylammonium pentacarbonyl(1-oxopentyl)chromate(1−) (**3**) (1.755 g, 5.00 mmol) and benzenemethanol (1.035 mL, 10.0 mmol) in Et_2O (20 mL) was reacted with HCl (15.0 mL, 15.00 mmol, 1 M in Et_2O) and CO as described above. Irradiation (20 h), extraction, and chromatography, using, in sequence, pentane−Et_2O (8:2), pentane−Et_2O (7:3), and pentane−Et_2O (1:1), gave, in order of elution, **16** (381 mg, 1.34 mmol, 27%) and **15** (20 mg, 0.09 mmol, 2%) as colorless liquids.

A similar reaction of tetramethylammonium pentacarbonyl(1-oxopentyl)tungstate(1−)[40] (**3**) (438 mg, 1.00 mmol) and benzenemethanol (0.52 mL, 5.00 mmol) in Et_2O (20 mL) with HCl (5.0 mL, 5.00 mmol, 1 M in Et_2O) and CO as described above gave, after irradiation (20 h), extraction, and chromatography using, in sequence, pentane−Et_2O (8:2), pentane−Et_2O (7:3), and pentane−Et_2O (1:1), a small amount of **16** together with $W(CO)_6$.

Methyl 2-Hydroxyhexanoate (17). A solution of tetramethylammonium pentacarbonyl(1-oxopentyl)chromate(1−)

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[32] The Aldrich Library of ^{13}C and ^1H FT-NMR Spectra # **2**,1220 A, and The Aldrich Library of FT-IR Spectra # **2**, 281 C.

[33] The Aldrich Library of ^{13}C and ^1H FT-NMR Spectra # **2**,1221 A, and The Aldrich Library of FT-IR Spectra # **2**, 271 C.

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[35] The Aldrich Library of ^{13}C and ^1H FT-NMR Spectra # **1**,1033 C, and The Aldrich Library of FT-IR Spectra # **1**, 659 B.

[36] The formation of a pink suspension in place of a faint yellow solution was observed in all cases where an acetal was formed. Upon addition of water, the suspension dissolves and changes color producing a light green aqueous phase.

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(**3**) (351 mg, 1.00 mmol) in methanol (20 mL) was reacted with HCl (5.0 mL, 5.00 mmol, 1 M in Et_2O) and CO as described above. Irradiation (20 h), extraction, and chromatography using pentanes−Et_2O (7:3) gave **17** (137 mg, 0.62 mmol, 62%) as a colorless oil. Spectroscopic data were in complete accordance with literature values.[41]

Methyl 2-Hydroxy-3-methylpentanoate (18). A solution of tetramethylammonium pentacarbonyl(2-methyl-1-oxobutyl)-chromate(1−)[42] (**4**) (351 mg, 1.00 mmol) in methanol (20 mL) was reacted with HCl (5.0 mL, 5.00 mmol, 1 M in Et_2O) and CO as described above. Irradiation (20 h), extraction, and chromatography using pentane−Et_2O (7:3) followed by pentanes−Et_2O (1:1) gave **18** (43 mg, 0.29 mmol, 29%, *SS*,*RR*:*SR*,*RS*, 4.1:1) as a colorless oil. Spectroscopic data were in complete accordance with literature values.[43]

Tetramethylammonium Pentacarbonyl(1-oxo-3-phenylpropyl)chromate(1−) (5). To a −78 °C cold solution of (2-iodoethyl)benzene (3.62 mL, 25.0 mmol) in Et_2O (50 mL) was added *tert*-butyllithium (30.0 mL, 50.0 mmol, 1.7 M in hexanes) *via* a cannula. The solution was stirred for 1 h producing a dark yellow solution, which was transferred *via* a cannula to a 0 °C cold slurry of $Cr(CO)_6$ (5.50 g, 25.0 mmol) in Et_2O (100 mL). After the solution was stirred for 1 h, the solvents were removed from the formed brown reaction mixture. The resulting brown solid residue was treated with a solution of tetramethylammonium bromide (7.70 g, 50.0 mmol) in degassed, distilled 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 **5** (5.23 g, 13.1 mmol, 52%) as yellow crystals: mp 68 °C; ^{1}H NMR δ 7.30−7.10 (m, 5 H), 3.27 (br s, 12 H) overlapping 3.23 (t, J = 7.5 Hz, 2H), 2.67 (t, J = 7.3 Hz, 2H); ^{13}C NMR (DMSO-d_6) δ 284.8 (+), 228.0 (+), 223.8 (+), 143.3 (+), 128.2 (−), 128.1 (−), 125.2 (−), 67.7 (+), 54.9 (−), 29.9 (+); IR (film) 2027, 1870 cm^{-1}.

Methyl 2-Hydroxy-4-phenylbutanoate (19) and 1,1-Dimethoxy-3-phenylpropane (20). A solution of tetramethylammonium pentacarbonyl(1-oxo-3-phenylpropyl)chromate (**5**) (399 mg, 1.00 mmol) in methanol (20 mL) was reacted with HCl (5.0 mL, 5.00 mmol, 1 M in Et_2O) and CO as described above. Irradiation (20 h), extraction, and chromatography using, in sequence, hexanes−EtOAc (8:2), hexanes−EtOAc (7:3), and hexanes−EtOAc (1:1) gave, in order of elution, **20** (48 mg, 0.27 mmol, 27%) and **19** (42 mg, 0.22 mmol, 22%) both as colorless liquids. Spectroscopic data of **19**[44] and **20**[45] were in complete accordance with literature values.

Benzyl 2-Hydroxy-2-cyclopropylacetate (21) and 1,1′-[Cyclopropylmethylidene bis(oxymethylene)]bis(benzene) (22). A solution of tetramethylammonium pentacarbonyl-(cyclopropylcarbonyl)chromate(1−)[46] (**6**) (335 mg, 1.00 mmol) and benzenemethanol (0.52 mL, 5.00 mmol) in Et_2O (20 mL) was reacted with HCl (5.0 mL, 5.00 mmol, 1 M in Et_2O) and CO as described above. Irradiation (20 h), extraction, and chromatography using hexanes−EtOAc (1:1) followed by hexanes−EtOAc (3:7) gave, in order of elution, **22** (52 mg, 0.20 mmol, 20%) and **21** (8 mg, 0.04 mmol, 4%) as colorless liquids. Partial spectroscopic data for **21**: ^{1}H NMR δ 7.36 (m, 5H), 5.25 (m, 2H), 3.82 (d, J = 6.7 Hz, 1H), 2.70 (br s, 1H), 1.36−0.40 (m, 5H); ^{13}C NMR δ 174.7, 135.3, 128.6, 128.4, 128.1, 72.4, 67.1, 14.8, 1.8, 1.7; IR (neat) 3087, 3009, 2961, 1737, 1265, 1211, 1082, 750, 698 cm^{-1}. Spectroscopic data for **22**: ^{1}H NMR δ 7.37−7.30 (s, 10H), 4.77 (d, J = 11.7 Hz, 2H), 4.62 (d, J = 11.7 Hz, 2H), 4.35 (d, J = 5.7 Hz, 1H), 1.36−0.40 (m, 5H); ^{13}C NMR δ 138.4 (+), 128.35 (−), 127.7 (−), 127.5 (−), 103.5 (−), 67.1 (+), 13.5 (−), 1.8 (+); IR (film) 3030, 2927, 2871, 1453, 1098, 1043, 1025, 735, 698 cm^{-1}.

Methyl 2-Hydroxy-2-cyclopropylacetate (23) and [Dimethoxymethyl]cyclopropane (24). A solution of tetramethylammonium pentacarbonyl(cyclopropylcarbonyl)chromium(1−) (**6**) (1.675 g, 5.00 mmol) in methanol (100 mL) was reacted with HCl (25.0 mL, 25.0 mmol, 1 M in Et_2O) and CO as described above. Irradiation (20 h), extraction, and chromatography using pentane−Et_2O (7:3) followed by pentane−Et_2O (1:1) gave, in order of elution, **24** (46 mg, 0.40 mmol, 8%) and **25** (120 mg, 0.95 mmol, 19%) as colorless liquids. Spectroscopic data of **23**[47] and **24**[48] were in complete accordance with literature values.

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