Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Mallinckrodt Chemical Co. for support of this research. We also thank Dr. Lee M. Daniels of the Iowa State Molecular Structure Laboratory for the crystallographic analysis of $Pd(dppp)_2$ by X-ray means.

Supplementary Material Available: Tables of complete bond distances and angles, positional parameters, general displacement parameters, and calculated hydrogen atom positions (7 pages). Ordering information is given on any current masthead page.

OM920119J

Oxidative Cleavage of Tetramethylammonium Pentacarbonyl(1-oxyalkylidene)chromate(0) Complexes: Formation of Carboxylic Acid Derivatives

Björn C. Söderberg* and Brian A. Bowden

Department of Chemistry, University of South Alabama, Mobile, Alabama 36688

Received January 29, 1992

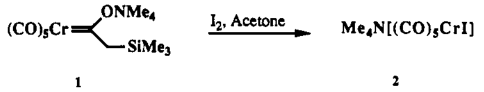
Reaction of tetramethylammonium pentacarbonyl(1-oxyalkylidene)chromate(0) complexes with iodine in the presence of a base and an alcohol afforded carboxylic acid esters in fair to good yield. Substituting an amine or water for the alcohol produced an amide or a carboxylic acid, respectively. The corresponding complexes of molybdenum and tungsten both gave comparable yields of ester product under the same conditions.

Introduction

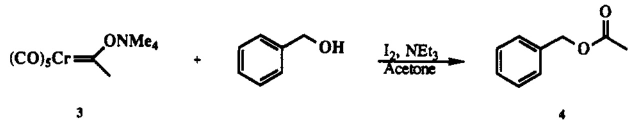
Metal acyl σ-bonds undergo facile cleavage by several reagents to form carboxylic acid derivatives.[1] For example, oxidation of nickel acylates $[RCONi(CO)_3X]$[2] and iron acylates $[RCOFe(CO)_4Na]$[3] with bromine or iodine affords carboxylic acids, esters, or amides, depending on the coreactant present in the reaction mixture. Other metal acylates formed in situ, such as those of palladium,[4] cobalt,[5] and nickel,[6] give esters and amides from alcohols and amines, respectively, without the help of an oxidizing reagent.

To our knowledge, the only example of such a reaction of chromium acylates is that reported by Connor and Jones. The authors isolated tetramethylammonium pentacarbonylchromium(I) iodide (2) in 85% yield as the sole product (Scheme I) upon reaction of tetramethylammonium pentacarbonyl[1-oxy-2-(trimethylsilyl)ethylidene]chromate(0) (1) with iodine in acetone.[7] No reports of organic products isolated from oxidative cleavage of tetramethylammonium pentacarbonyl(1-oxyalkylidene)chromate(0) complexes employing halogens have appeared.

Scheme I



Scheme II



The fate of the carbene ligand from reactions of 1-oxyalkylidene complexes such as 1 is of interest for our understanding and development of novel reactions thereof. As part of a program to develop new synthetic reactions of tetramethylammonium pentacarbonyl(1-oxyalkylidene)chromate(0) complexes,[8] we set out to examine their reactions with iodine or bromine in the presence of a nucleophile. In this paper we report a facile oxidative cleavage of a selected number of tetramethylammonium pentacarbonyl(1-oxyalkylidene)chromate(0) complexes to give carboxylic acid derivatives.

Results and Discussion

Addition of a slight excess of iodine (1.1 equiv) to a solution of tetramethylammonium pentacarbonyl(1-oxyethylidene)chromate(0) (3, 1.0 equiv), triethylamine (1.5 equiv), and benzyl alcohol (1.1 equiv) in acetone followed by stirring for 24 h gave a 58% yield of benzyl acetate (4) (Scheme II) after air oxidation (to remove any arene-bound chromium) and chromatography on a short silica gel column. Benzyl acetate was the only product observed by

---

[1] For reviews, see: (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Transition Metal Chemistry*; University Science Books: Mill Valley, CA; 1987. (b) Heck, R. F. *Adv. Catal.* **1977**, *26*, 323. (c) Cassar, L.; Chiusoli, G. P.; Guerrieri, F. *Synthesis* **1973**, 509.

[2] (a) Corey, E. J.; Hegedus, L. S. *J. Am. Chem. Soc.* **1969**, *91*, 1233. (b) Crandall, J. K.; Michaely, W. J. *J. Organomet. Chem.* **1973**, *51*, 375.

[3] (a) Collman, J. P. *Acc. Chem. Res.* **1975**, *8*, 342. (b) Collman, J. P.; Winter, S. R.; Komoto, R. G. *J. Am. Chem. Soc.* **1973**, *95*, 249. (c) Masada, H.; Mitzuno, M.; Suza, S.; Watanabe, Y.; Takegami, Y. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 3824. (d) Takegami, Y.; Watanabe, Y.; Masada, H.; Kanaya, I. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 1465.

[4] See ref 1a and: Heck, R. F. *Palladium Reagents in Organic Syntheses*; Academic Press: London, 1985.

[5] Heck, R. F. In *Organic Synthesis via Metal Carbonyls*; Wender, I., Pino, P., Eds.; Wiley: New York, 1968.

[6] (a) Heck, R. F. *Acc. Chem. Res.* **1969**, *2*, 10. (b) Guerrieri, F.; Chiusoli, G. P. *J. Organomet. Chem.* **1968**, *15*, 209. (c) Chiusoli, G. P. *Acc. Chem. Res.* **1973**, *6*, 442.

[7] Connor, J. A.; Jones, E. M. *J. Organomet. Chem.* **1973**, *60*, 77.

[8] Söderberg, B. C.; Turbeville, M. J. *Organometallics* **1991**, *10*, 3951.

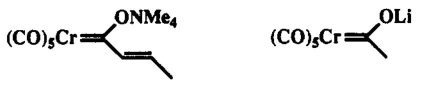
0276-7333/92/2311-2220$03.00/0

^{1}H NMR spectroscopy of the crude reaction mixture.

Several of the reaction parameters were varied in order to examine their influence on the reaction. Benzyl acetate was formed from 3 using the same ratio of reagents, in different solvents. Both polar and nonpolar solvents afforded similar isolated yields of benzyl acetate after 24 h: tetrahydrofuran (20%), dichloromethane (45%), acetonitrile (46%), ethyl acetate (24%), and dimethylformamide (33%). Even in hexane, in which the starting chromium complex 3 is insoluble, a 54% yield of 4 was isolated. No product was obtained when the reaction was performed in dimethyl sulfoxide, a solvent known to oxidize the carbon–chromium double bond of Fischer carbenes to a carbon–oxygen double bond.[9] Employing acetone as solvent and cutting the reaction time from 24 to 1 h gave a slightly lower yield of 4 (54%), as did reaction using 3 with 1.1 equiv of bromine as oxidant instead of iodine (1 h, 49%). Little change was noted upon increasing to 2 equiv of iodine (acetone, 1 h, 53%); however no product was obtained when a large excess (10 equiv) of iodine was employed. The latter result contrasts with the cleavage of related ironacyl complexes with iodine; there a 10-fold excess of iodine gave esters in excellent yield.[10] Iron alkyl complexes have been oxidatively cleaved by a number of reagents in the presence of carbon monoxide and an alcohol to produce esters. We briefly examined the reaction of 3 by substituting iodine for ceric ammonium nitrate (CAN) in acetonitrile in the presence of pyridine and benzyl alcohol. Although an immediate color change and evolution of carbon monoxide was observed, benzyl acetate was not observed in the crude reaction mixture (^{1}H NMR analysis).[11] The reaction of tetramethylammonium pentacarbonyl(1-oxyalkylidene)chromate(0) complexes with halides probably procedes via a different mechanism than that proposed by Rosenblum for the iron alkyl complexes.[12]

The importance of an added base was seen in the significant drop in yield from 54% to 28% of 4 in its absence (acetone, 1 h). Two different bases, triethylamine and pyridine, afforded essentially identical results. The use of excess benzyl alcohol substantially increased the yield of benzyl acetate (acetonitrile, 1 h) from 46% to 65%, but purification of the crude reaction mixture was complicated due to the residual alcohol.

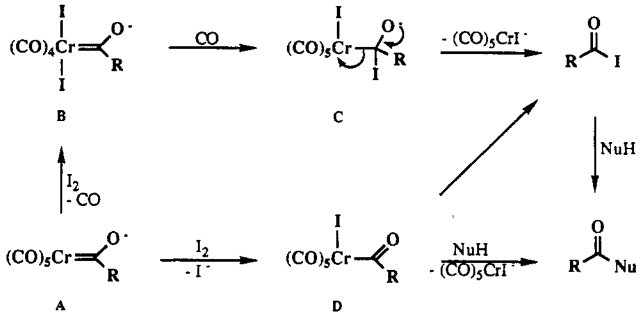
A number of different tetramethylammonium pentacarbonyl(1-oxyalkylidene)chromate(0) complexes, prepared by the addition of the appropriate lithium reagent to chromium hexacarbonyl followed by exchange of lithium by a tetramethylammonium cation, were treated with iodine in the presence of pyridine and a nucleophile (Table I). In addition to benzyl acetate (entry 1), benzyl esters were isolated from the reaction of oxyphenylmethylidene, 1-oxypentylidene, and 1-oxy-2-(trimethylsilyl)ethylidene complexes (entries 2–4, respectively) upon oxidation in acetonitrile in the presence of benzyl alcohol.[13] The latter product was somewhat of a surprise in the light of the findings of Connor and Jones.[7] Although a base was not employed in the reaction in Scheme I, it is probable that either (trimethylsilyl)acetic acid or acetic acid[14] was formed but was overlooked by the authors. Using phenol as nucleophile in place of benzyl alcohol afforded phenyl benzoate in 52% yield (entry 5).



5 6

Figure 1.

Scheme III



When the nucleophile was employed as solvent, methyl, isopropyl, and *tert*-butyl benzoate were isolated by oxidation of the tetramethylammonium pentacarbonyl(oxyphenylmethylidene)chromate(0) (entries 6–8) and methyl 2-furanoate by oxidation of the oxy(2-furyl)methylidene complex (entry 9). Although the yield decreased with the steric bulk of the nucleophile, a fair yield of *tert*-butyl benzoate was obtained.

Nucleophiles other than alcohols also efficiently formed carboxylic acid derivatives from tetramethylammonium pentacarbonyl(oxyphenylmethylidene)chromate(0). Thus, benzoic acid and *N*,*N*-diisopropylbenzamide were isolated in good yields by respective addition of water or diisopropylamine to the reaction mixture (entries 10 and 11). Finally, the tetramethylammonium pentacarbonyl(1-oxyethylidene)metalate(0) complexes of the remaining metals in group VIb, molybdenum and tungsten, both gave, under oxidative conditions identical to those described for chromium, a 51% yield of benzyl acetate (entries 12 and 13). In our hands, neither tetramethylammonium pentacarbonyl(1-oxy-2-butenylidene)chromate(0) (5) nor lithium pentacarbonyl(1-oxy-2-ethylidene)chromate(0) (6)[15] gave any products although they were both completely consumed during the reaction (Figure 1). The absence of any organic product after filtration and solvent removal of the latter crude reaction mixture is puzzling, although, upon addition of iodine to a THF solution of in situ prepared 6, a reaction in appearance very similar to that of the tetramethylammonium complex 3 occurred. The effect of the counterion, lithium versus tetramethylammonium, may be caused by the latter's inability, in contrast to lithium, to coordinate to the oxygen atom, leaving a naked more reactive anion.

A possible mechanism for the formation of carboxylic acid derivatives from tetramethylammonium pentacarbonyl(1-oxyethylidene)chromate(0) complexes is exemplified in Scheme III and is similar to that proposed for the oxidation of iron acyl complexes.[16] Loss of a carbonyl ligand followed by oxidative addition of iodine to A affords the chromium(II) intermediate B.[17] Migration of iodide and recoordination of CO (or a solvent molecule) affords

---

(9) For a few examples, see: (a) Casey, C. P.; Burkhardt, T. J.; Bunell, C. A.; Calagrese, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 2127. (b) Wulff, W. D.; Yang, D. C. *J. Am. Chem. Soc.* **1983**, *105*, 6726. (c) Chan, K. S.; Wulff, W. D. *J. Am. Chem. Soc.* **1986**, *108*, 5299. (d) Wulff, W. D.; Anderson, B. A.; Toole, A. J. *J. Am. Chem. Soc.* **1989**, *111*, 5485.

(10) Collman, J. P.; Winter, S. R.; Komoto, R. G. *J. Am. Chem. Soc.* **1973**, *95*, 249.

(11) This experiment was proposed by one of the reviewers.

(12) Rosenblum, M. *Acc. Chem. Res.* **1974**, *7*, 122.

(13) Acetonitrile was perceived to be the best solvent for the oxidative cleavage due to a somewhat more facile workup.

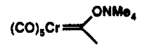
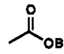
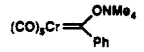
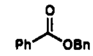
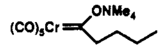
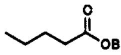
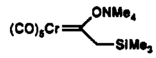
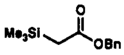
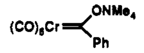
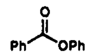
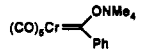
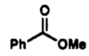
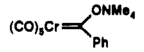
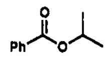
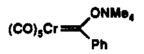
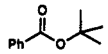
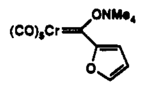
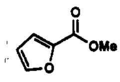
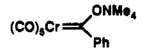
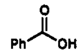
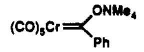
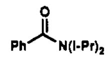
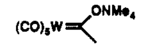
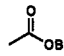
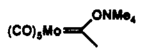
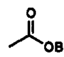
(14) By acid cleavage of benzyl (trimethylsilyl)acetate.

(15) Complex 6 was prepared and reacted *in situ* in tetrahydrofuran.

(16) Winter, S. R. Ph.D. Thesis, Stanford University, 1973.

(17) A related diiodotungsten carbene complex has been isolated: Lappert, M. F.; Pye, P. L. *J. Chem. Soc., Dalton Trans.* **1977**, 1283. This was brought to our attention by one of the referees.

Table I. Formation of Carboxylic Acid Derivatives from Tetramethylammonium Pentacarbonyl[1-oxyalkylidene]metalate(0) Complexes

entry	complex[a]	nucleophile	product	yield[b]
1		BnOH		46 %
2		BnOH		60 %
3		BnOH		29 %
4		BnOH		16 %
5		PhOH		52 %
6		MeOH		77 %
7		i-PrOH		65 %
8		t-BuOH		49 %
9		MeOH		68 %
10		H_2O		75 %
11		$(i\text{-}Pr)_2NH$		69 %
12		BnOH		51 %
13		BnOH		51 %

[a] All reactions were performed with isolated complex as described in the Experimental Section. [b] Refers to pure isolated compounds.

the complex C that is cleaved, forming an acyl iodide and $(CO)_5CrI^-$ or $(solvent)(CO)_4CrI^-$. The acyl iodide rapidly reacts with any nucleophile present in the reaction mixture to give a carboxylic acid derivative. A somewhat different mechanism was proposed by one of the reviewers (Scheme III). Reaction of complex A with iodine forms the acyl iodo complex D followed by cleavage of the metal–carbon bond either by an iodide anion to form an acyl iodide or directly by a nucleophile to give the expected product. At this point we favor the former mechanism in that, in addition to the two products, the formation of carbon monoxide, observed in most but not all of the cases previously discussed, is also explained. Hydrogen iodide, or hydrogen bromide in the case where bromine was used, formed in the reaction is removed from the reaction mixture by the added base, thus minimizing unwanted side reactions.

A free carbene was proposed by Connor as an intermediate in the reaction of 1 with iodine.[7] We did not find any evidence of a carbene in any of our reactions either as such or trapped by the nucleophile present in the reaction mixture. No further information on the mechanism, such as the observation of intermediates, was obtained upon iodine oxidation of 3 in acetone-d_6 in the absence of an alcohol trap.

In summary, we have shown that tetramethylammonium pentacarbonyl(1-oxyalkylidene)metalate(0) complexes of group VIb are readily cleaved by either iodine or bromine in the presence of a nucleophile to afford carboxylic acid derivatives.

Experimental Section

Materials. The tetramethylammonium pentacarbonyl(1-oxyalkylidene)metalate(0) complexes were prepared according to literature procedures: tetramethylammonium pentacarbonyl(1-oxyethylidene)chromate(0),[18] tetramethylammonium pentacarbonyl(oxyphenylmethylidene)chromate(0),[18] tetramethylammonium pentacarbonyl(1-oxypentylidene)chromate(0),[19] tetramethylammonium pentacarbonyl[1-oxy-2-(trimethylsilyl)ethylidene]chromate(0),[8] tetramethylammonium pentacarbonyl[oxy(2-furyl)methylidene]chromate(0),[20] tetramethylammonium pentacarbonyl(1-oxyethylidene)molybdate(0),[18] tetramethylammonium pentacarbonyl(1-oxyethylidene)tungstate(0),[18] tetramethylammonium pentacarbonyl(1-oxy-2-butenylidene)chromate(0).[21] All other reagents and solvents (anhydrous) were obtained from commercial sources; the solvents were stored over 4-Å molecular sieves. Diethyl ether and tetrahydrofuran were distilled from benzophenone ketyl prior to use.

All isolated carboxylic acid derivatives except benzyl (trimethylsilyl)acetate are commercially available, and spectroscopic data were in accordance with literature values. The commercially available products have not been referenced below.

Benzyl Acetate (Method A). To a solution of 309 mg (1.00 mmol) of tetramethylammonium pentacarbonyl(1-oxyethylidene)chromate(0), 121 μL (1.50 mmol) of pyridine, and 207 μL (2.00 mmol) of benzyl alcohol in 10 mL of acetonitrile, at ambient temperature, was added 508 mg (2.00 mmol) of solid iodine. Upon addition the color changed within seconds to a deep brown-red and carbon monoxide evolution was observed.[22] The reaction mixture was stirred for 160 min, and a teaspoon of silica gel was added followed by solvent removal on a rotary evaporator at water aspirator pressure. The solid residue was put on top of a 7- × 2-cm silica gel column and the column was eluted with first 50 mL of hexane followed by 75 mL of hexane/ethyl acetate (9:1) to give a yellow solution. The solution was air oxidized (sunlight) for 5 h to remove any arene-bound chromium.[23] The clear colorless solution with a green precipitate was filtered through a 0.5-cm pad of Celite, the pad was washed with hexane/ethyl acetate (9:1), and the solvents were removed on a rotary evaporator to give 103 mg of a colorless oil. The oil was flash chromatographed on a 17- × 3-cm column eluted with hexane/ethyl acetate (9:1) to give 69 mg (0.46 mmol, 46%) of benzyl acetate as a colorless oil.

---

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

(19) From chromium hexacarbonyl and *n*-butyllithium followed by treatment of the intermediate lithium complex with tetramethylammonium chloride as described by Fischer and Maasböl in ref 18.

(20) Connor, J. A.; Jones, E. M. *J. Chem. Soc. A* **1971**, 1974.

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

(22) In several experiments a slight exothermic reaction together with evolution of carbon monoxide was observed.

(23) In the absence of sunlight, a Conrad-Hanovia 7825 medium-pressure mercury lamp (Pyrex well) can be used, although the oxidation appears to be faster in direct sunlight. The oxidation was continued until a clear colorless solution was obtained.

The following compounds were prepared according to method A by the reaction of 1.00 mmol of tetramethylammonium pentacarbonyl(1-oxy-1-alkylidene)metalate(0) complex, 121 μL (1.50 mmol) of pyridine, and 508 mg (2.00 mmol) of iodine in 10 mL of acetonitrile with the appropriate nucleophile, as described above with some modifications.

Benzyl Benzoate. Reaction of 371 mg (1.00 mmol) of tetramethylammonium pentacarbonyl(oxyphenylmethylidene)chromate(0) with 207 μL (2.00 mmol) of benzyl alcohol, for 140 min, gave, after air oxidation (4 h) and chromatography (hexane/ethyl acetate, 4:1), 128 mg (0.64 mmol, 60%) of benzyl benzoate as a colorless oil.

Benzyl Pentanoate. Reaction of 351 mg (1.00 mmol) of tetramethylammonium pentacarbonyl(1-oxypentylidene]chromate(0) with 207 μL (2.00 mmol) of benzyl alcohol, for 110 min, gave, after air oxidation (4 h) and chromatography (hexane/ethyl acetate, 9:1), 55 mg (0.29 mmol, 29%) of benzyl pentanoate as a colorless oil.

Benzyl (Trimethylsilyl)acetate.[24] Reaction of 381 mg (1.00 mmol) of tetramethylammonium pentacarbonyl(1-oxypentylidene)chromate(0) with 207 μL (2.00 mmol) of benzyl alcohol, for 130 min, gave, after air oxidation (80 min) and chromatography (hexane/ethyl acetate, 9:1), 36 mg (0.16 mmol, 16%) of benzyl (trimethylsilyl)acetate as a colorless oil.

Phenyl Benzoate. Reaction of 371 mg (1.00 mmol) of tetramethylammonium pentacarbonyl(oxyphenylmethylidene)chromate(0) with 188 mg (2.00 mmol) of phenol, for 140 min, gave, after air oxidation (3 h) and chromatography (hexane/ethyl acetate, 9:1), 102 mg (0.52 mmol, 52%) of phenyl benzoate as a colorless oil.

***N,N*-Diisopropylbenzamide.** Reaction of 371 mg (1.00 mmol) of tetramethylammonium pentacarbonyl(oxyphenylmethylidene)chromate(0) with 490 μL (3.50 mmol) of diisopropylamine,[25] for 100 min, gave, after air oxidation (8 h) and chromatography (hexane/ethyl acetate, 4:1), 141 mg (0.69 mmol, 69%) of *N,N*-diisopropylbenzamide as white crystals.

Benzyl Acetate (from Molybdenum Complex). Reaction of 353 mg (1.00 mmol) of tetramethylammonium pentacarbonyl(1-oxyethylidene)molybdate(0) with 207 μL (2.00 mmol) of benzyl alcohol, for 140 min, gave, after air oxidation (1.5 h) and chromatography (hexane/ethyl acetate, 9:1), 77 mg (0.51 mmol, 51%) of benzyl acetate as a colorless oil.

Benzyl Acetate (from Tungsten Complex). Reaction of 441 mg (1.00 mmol) of tetramethylammonium pentacarbonyl(1-oxyethylidene)tungstate(0) with 207 μL (2.00 mmol) of benzyl alcohol, for 140 min, and filtering through a 7- × 2-cm silica gel column, as described above, gave a colorless solution. The solvents were removed without air oxidation, and 246 mg of colorless oil together with crystalline tungsten hexacarbonyl was obtained. The crude product was flash chromatographed (hexane/ethyl acetate, 9:1) to afford 77 mg (0.51 mmol, 51%) of benzyl acetate as a colorless oil.

Methyl Benzoate (Method B). To a solution of 371 mg (1.00 mmol) of tetramethylammonium pentacarbonyl(oxyphenylmethylidene)chromate(0) and 121 μL (1.50 mmol) of pyridine in 10 mL of methanol, at ambient temperature, was added 279 mg (1.10 mmol) of iodine(s). Upon addition the color changed, within seconds, to a deep brown-red and some gas evolution was observed. The reaction mixture was worked up as described in method A. After air oxidation (60 min) and chromatography (hexane/ethyl acetate, 4:1), 105 mg (0.77 mmol, 77%) of methyl benzoate was isolated as a colorless oil.

The following compounds were prepared according to method B by the reaction of 1.00 mmol of tetramethylammonium pentacarbonyl(1-oxy-1-alkylidene)chromate(0) complex, 121 μL (1.50 mmol) of pyridine, and 508 mg (2.00 mmol) of iodine(s) in 10 mL of the appropriate nucleophilic solvent as described above with some modifications.

Isopropyl Benzoate. Reaction of 371 mg (1.00 mmol) of tetramethylammonium pentacarbonyl(oxyphenylmethylidene)chromate(0) in 10 mL of isopropyl alcohol, for 130 min, gave, after short-column chromatography (hexane/ethyl acetate, 4:1), air oxidation (110 min), and Celite filtration, 106 mg (0.65 mmol, 65%) of isopropyl benzoate as a very faint yellow oil.[26]

***tert*-Butyl Benzoate.** Reaction of 371 mg (1.00 mmol) of tetramethylammonium pentacarbonyl(oxyphenylmethylidene)chromate(0) in 10 mL of *tert*-butanol, for 150 min at 30 °C, gave, after short-column chromatography (hexane/ethyl acetate, 4:1), air oxidation (130 min), and Celite filtration, 87 mg (0.49 mmol, 49%) of *tert*-butyl benzoate as a faint yellow oil.[26]

Methyl 2-Furanoate. Reaction of 361 mg (1.00 mmol) of tetramethylammonium pentacarbonyl(oxy(2-furyl)methylidene]chromate(0) in 10 mL of methanol, for 4.5 h, gave, after short-column chromatography (hexane/ethyl acetate, 4:1), air oxidation (60 min), and Celite filtration, 86 mg (0.68 mmol, 68%) of methyl 2-furanoate as a pale yellow oil.[26]

Benzoic Acid. To a solution of 371 mg (1.00 mmol) of tetramethylammonium pentacarbonyl(1-oxyethylidene]chromate(0), 121 μL (1.50 mmol) of pyridine, and 900 μL (50.0 mmol) of water in 10 mL of acetonitrile, at ambient temperature, was added 508 mg (2.00 mmol) of iodine (s). Upon addition the color changed within seconds to a deep brown-red and some gas evolution was observed. The reaction mixture was stirred for 120 min, 6 mL of 1 M HCl (aq) was added, and the red solution was extracted with three 25-mL portions of diethyl ether. To the combined organic phase was added solid sodium bisulfite until a colorless solution was obtained. The solution was dried (MgSO$_4$), filtered, and evaporated to dryness, affording 91 mg (0.75 mmol, 75%) of benzoic acid as faint yellow crystals.

Acknowledgment. This research was supported by the University of South Alabama in the form of a startup grant to B.C.S.

OM920050F

---

[24] Emde, H.; Simchen, G. *Synthesis* 1977, 867.

[25] No pyridine was added.

[26] A second chromatography was not necessary.