Hypervalent Iodine Oxidation of Silyl Enol Ethers under Lewis Acid Conditions in Methanol. A General Route to α-Methoxy Ketones

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Hypervalent iodine oxidation of various silyl enol ethers (aromatic, heteroaromatic, aliphatic) using iodosobenzene–boron trifluoride etherate in methanol leads to α-methoxylation of ketones in high yields. The scope and mechanism of the reaction are discussed.

α-Methoxy ketones are important synthetic intermediates that are frequently prepared either by the reaction of α-diazo ketones with methanol and boron trifluoride etherate (eqn 1)[1] or by the reaction of arylmagnesium

$$RC(=O)CHN_2 + MeOH \xrightarrow{BF_3\cdot Et_2O} RCOCH_2OMe \quad (1)$$

$$RMgBr + CNCH_2OMe \rightarrow RCOCH_2OMe \quad (2)$$

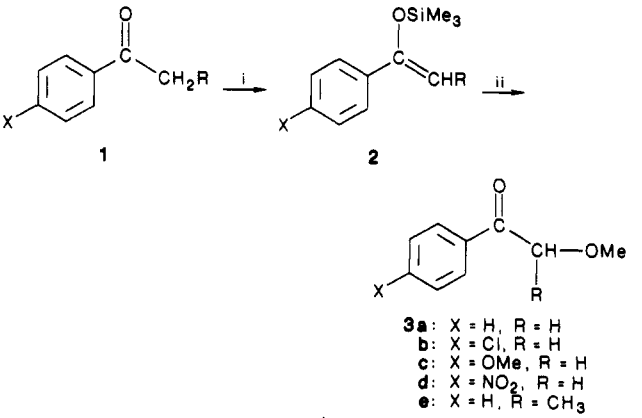
bromide with methoxyacetonitrile (eq 2).[2,3] In a continuation of our study on the synthetic utility of hypervalent iodine reagents,[4] we now report a direct and general route for the α-methoxylation of various ketones.[5] Our approach is based on the hypervalent iodine oxidation of silyl enol ethers, which has been used by us for the synthesis of α-hydroxy ketones.[6] Various acetophenones (**1a–1d**) and propiophenone (**1e**) were converted into the corresponding silyl enol ethers (**2a–2e**) by the method of House et al.[7] In the initial studies we used a CH_2Cl_2–MeOH solvent system, and oxidation of **2** using 1.1 equiv of iodosobenzene, boron trifluoride etherate (3 equiv), and an excess of methanol in dichloromethane or ether at −50 °C afforded α-methoxy ketones **3a–3e**[5] (Scheme I).

These conditions did not give reproducible yields of products **3a–3d**, and variable amounts of 1,4-diketones (coupling product[8]) were also formed. In the case of propiophenone (**1e**) the methoxy ketone **3e** was obtained in only 10% yield. It was impractical to increase the amount of iodosobenzene because of its limited solubility in dichloromethane or ether. We found that iodosobenzene was quite soluble in methanol at room temperature. Addition of boron trifluoride etherate gives a solution of iodosobenzene in methanol even at −70 °C. The optimum conditions for oxidizing silyl enol ethers **2a–2e** are 1.0 equiv of silyl enol ether, 1.1 equiv of iodosobenzene, and 2 equiv of boron trifluoride etherate in methanol at −70 °C. Under these conditions oxidation of silyl enol ethers occurs smoothly with the formation of α-methoxy ketones **3a–3e** in very high yields (Table I).

The reaction was further extended to 2-acetylpyridine (**4**) and 2,6-diacetylpyridine (**5**) and oxidation of silyl enol ethers **6** and **7** occurred in good yield using methanol–dichloromethane (1:50). In the latter case (**7**) the ratio of silyl enol ether, iodosobenzene, boron trifluoride etherate, and methanol used was 1:2:4:10.

Among the other heterocyclic ketones we studied, silyl enol ethers of 2-acetylfuran (**10**) and 2-acetylthiophene (**11**)

Scheme I[a]



[a] Key: i = Me_3SiCl, Et_3N–DMF; ii = $(C_6H_5IO)_n$, $BF_3\cdot Et_2O$, CH_3OH.

underwent α-methoxylation without difficulty when methanol was used as a solvent whereas use of methanol–dichloromethane did not give acceptable yields of the products **12** and **13**. The reaction is sensitive to temperature; e.g. if this reaction is carried out at higher temperatures, a considerable amount of side product is formed such as methyl aryl acetates obotained by a 1,2 aryl shift. Therefore, it is advisable to leave the mixture at −70 °C for about 1 h and then slowly allow the reaction mixture to room temperature (during 2 h). These conditions gave maximum yields of the products on a wide variety of ketones.

This method works well for α-methoxylation of aliphatic ketones. Thus, with methanol as a solvent, cyclohexanone silyl enol ether **14** and the sterically hindered molecule *tert*-butyl methyl ketone (pinacolone) silyl enol ether **15**

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(1) Newman, M. S.; Beal, P. F. *J. Am. Chem. Soc.* **1950**, *72*, 5161.
(2) Pratt, D. D.; Robinson, R. *J. Chem. Soc.* **1923**, 745.
(3) 1-Tetralone is converted with thallium trinitrate/K-10 to 1:1 mixture of methyl indan-1-carboxylate and 2-methoxy-1-tetralone. This method is not general for obtaining α-methoxy ketones. See: Taylor, E. C.; Chiaryl, C. S.; McKillop, A.; White, J. F. *J. Am. Chem. Soc.* **1976**, *98*, 6750.
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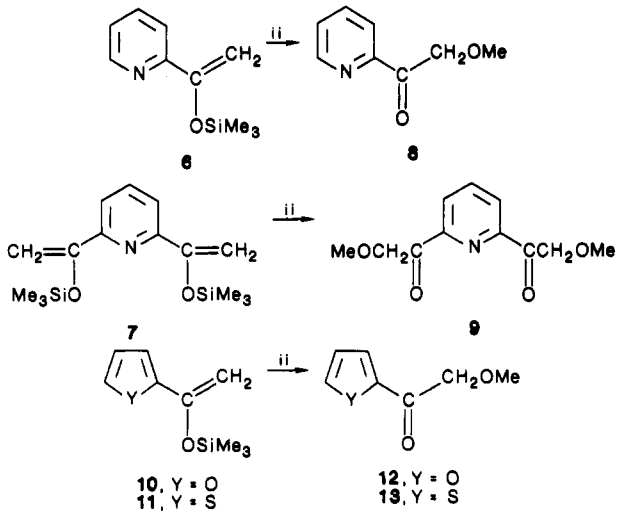
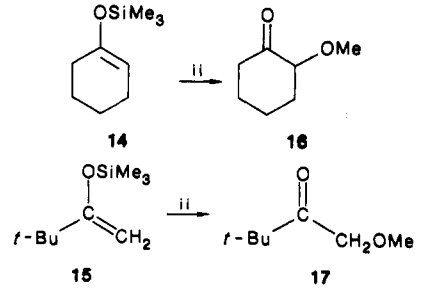


Table I. Methoxy (and Alkoxy) Ketones 1, 7, and 8 Prepared by the Hypervalent Iodine Oxidation of Silyl Enol Ethers

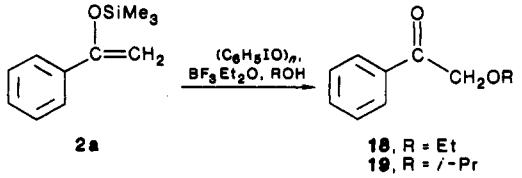
product	yield,[a] %	mp/bp, °C	mol formula or reported mp/bp, °C
3a	78	119–121 (15 mm)	118–120 (15 mm)[2]
3b	76	64–65[c]	60[15]
3c	71	39–40	39.5–40.5[1]
3d	68	119–120	118–119,[13] 121[14,15]
3e	75	*f*	78–80 (1 mm)[16]
8	70	82–83 (0.05 mm)	$C_8H_9NO_2$[d]
9	71	101–102	$C_{11}H_{13}NO_4$[d]
12	60[b]	66–68 (0.01 mm)	$C_7H_8O_3$[d]
13	54[b]	59–62 (0.01 mm)	$C_7H_8O_2S$[d]
16	78	186–187	185 (750 mm)[e]
17	85	52–53 (10 mm)	52 (10 mm)[17]
18	80	123–125 (10 mm)	125–127 (11 mm)[1]
19	45	87–88 (2 mm)	87 (2 mm)[1]

[a] Yield of isolated pure product with respect to the quantity of silyl enol ether used. The actual yields (calculated from ^{1}H NMR of crude product) were between 80 and 96%. [b] Column chromatographic separation of crude product using hexane–ether (9:1) as eluant on silica gel gave much better results than distillation. [c] Crystallized by addition of methanol to the crude mixture followed by cooling to 0 °C. [d] For analyses and spectral data see the Experimental Section. [e] Commercially available from Aldrich. [f] Separated by column chromatography and characterized by ^{1}H NMR.

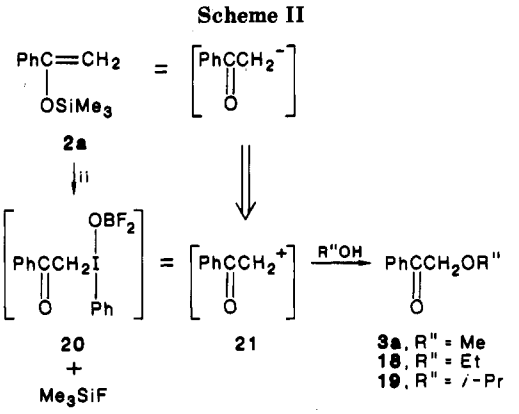
were converted into corresponding α-methoxy ketones **16** and **17** in almost quantitative yields.



Furthermore, we carried out the oxidation of acetophenone silyl enol ether using ethanol and isopropyl alcohol (instead of methanol) and found that α-ethoxyacetophenone (**18**) and α-isopropoxyacetophenone (**19**) are



Scheme II



formed in good yield. It should be noted that neither alcohol functional group was oxidized to the ketone or aldehyde. However, the use of benzyl alcohol did not give corresponding α-benzyloxy ketone in acceptable yields; benzyl alcohol itself is oxidized to benzaldehyde under various conditions attempted by us.

Thus, the oxidative conversion of silyl enol ethers to the corresponding α-methoxy ketones is significant for the following reasons: (a) α-Methoxy ketones are obtained in a single step, and the procedure is very simple. (b) 2-[(Methoxymethyl)carbonyl]pyridine (**8**) and 2,6-bis-[(methoxymethyl)carbonyl]pyridine (**9**) are potentially valuable intermediates for the synthesis of their corresponding oximes, which are useful acetylcholinesterase reactivators,[9] and corresponding thiosemicarbazones, which were prepared as antimalarial agents.[10] (c) The N atoms in compounds **6** and **7** and S atom in **11** are not oxidized under the reaction conditions. (d) Yields of the products are generally high (Table I). (e) The method works on a wide variety of ketones and therefore is a general method for α-methoxylation of ketones.

The structures of products known in literature are based upon comparison with the reported data. New compounds were characterized by microanalyses and spectral data (MS, IR, ^{1}H NMR). The characteristic feature in the ^{1}H NMR spectrum of the α-methoxy ketone is the appearance of two singlets at δ 4.5–5.05 and around δ 3.40, respectively, due to the methylene group protons (adjacent to ketone and α-methoxy group protons.

A reasonable pathway for the present α-methoxylation reaction involves the addition of the electrophile $C_6H_5I^+$-OB^-F_3 [generated from $(C_6H_5IO)_n$ and BF_3] to enol derivative **2a** to give intermediate **20**, which is the synthetic equivalent of carbocation **21** (Scheme II). This sequence may be viewed as umpolung of an enolate anion. The reaction is completed by nucleophilic addition of alcohol to yield α-alkoxy ketone. It is worth mentioning that the proposed intermediate **20**, in principle, could yield three different products, namely α-methoxy ketone **3a** (as presently found), α-hydroxy ketone dimethyl acetal **22** [as found using $PhCOCH_3$–$(C_6H_5IO)_n$, KOH–CH_3OH],[11] and rearranged product methyl phenylacetate (**23**) (as found using $PhCOCH_3$, $C_6H_5I^+OHOTs^-$, MeOH at room temperature)[12] as shown in Scheme III.

(9) The results of acetylcholinesterase reactivation studies will be published elsewhere.

(10) The antimalarial properties of these compounds are being studied and will be published separately.

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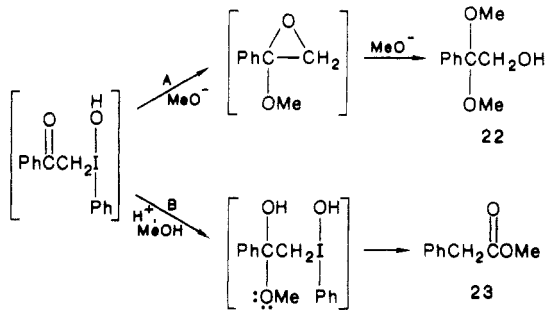
Scheme III



Under basic conditions and in the presence of the nucleophile $^{-}OCH_3$, attack at the carbonyl group with rate-limiting intramolecular oxide formation (A) occurs.[11] In route B the hemiketal intermediate formed under room-temperature conditions apparently is a prerequisite for rearrangement.[12] In a separate experiment **3a** was not converted to **23** with BF_3-Et_2O-MeOH at room temperature.

In conclusion, the present hypervalent iodine oxidative method provides an excellent method for direct α-methoxylation of aromatic, heterocyclic, and aliphatic ketones.

Experimental Section

Melting points were determined on a Thomas capillary melting point apparatus and are uncorrected. The IR spectra were obtained on a Unicam SP1000 IR spectrophotometer, and peak positions are expressed in reciprocal centimeters. ^1H NMR spectra were recorded at 60 MHz with a Varian A60 or EM-360 spectrometer using Me_4Si as an internal standard. Mass spectra were scanned with Hewlett-Packard GC/MS 5985 apparatus at 70 eV.

All ketones, iodobenzene, chlorotrimethylsilane, and triethylamine were obtained from Aldrich. Fresh boron trifluoride etherate (Aldrich) was used.

Iodosobenzene was prepared by oxidation of iodobenzene with peracetic acid followed by hydrolysis with aqueous sodium hydroxide.[18]

Silyl Enol Ethers. The silyl enol ethers **2a–2e**, **6**, **7**, **10**, **11**, **14**, and **15** were prepared from the respective ketones according to the general method A of House et al.[7] However, dilute hydrochloric acid was not used in the workup, because acid hydrolysis of the silyl enol ethers occurred to a significant extent in some cases. The ratio of the reactants was the same (as in ref 7) in the case of monoketones, but a double amount of chlorotrimethylsilane and triethylamine was used in the preparations that start from a diketone, 2,6-diacetylpyridine (**5**). All silyl enol ethers were distilled before use.

Preparation of 2,6-Diacetylpyridine Bis(silyl enol ether) (7). To a solution of 32.60 g (0.30 mol) of chlorotrimethylsilane and 60.60 g (0.60 mol) of triethylamine in 200 mL of dimethylformamide was added 2,6-diacetylpyridine (**5**; 20.38 g, 0.125 mol). The resulting mixture was refluxed with stirring overnight and then cooled, diluted with 400 mL of pentane, and washed with three 300-mL portions of ice-cold aqueous sodium bicarbonate. The aqueous layer was extracted with pentane (2 × 150 mL), and the combined organic phase was washed with cold aqueous sodium chloride solution (200 mL). The resulting pentane solution was dried and concentrated in vacuo to yield crude silyl enol ether, 92%. Distillation gave pure product: bp 129–131 °C (0.05 mm); 29.5 g (77%); ^1H NMR ($CDCl_3$) δ 1.02 (s, 18 H), 4.53 (s, 2 H), 5.76 (s, 2 H), 7.56 (m, 3 H).

General Procedure for the Preparation of Methoxymethyl Ketones 1. Iodosobenzene (4.84 g, 0.022 mol) was dissolved in absolute methanol (100 mL), and boron trifluoride etherate (5.67 g, 0.040 mol) was added. The mixture was stirred and cooled to −70 °C, and then the silyl enol ether (0.020 mol) was added. The mixture was stirred at −70 °C for 1 h, and then the temperature was slowly raised (2 h) to room temperature. Stirring was continued for another 30 min, and then the methanol was evaporated in vacuo. Water (100 mL) was added,[19] and the resulting mixture was neutralized with 5% aqueous sodium bicarbonate. The aqueous mixture was transfered to a separatory funnel and extracted with dichloromethane (3 × 50 mL). The organic phases were combined, dried with magnesium sulfate, and concentrated in vacuo to yield crude product. Final isolation and purification were done by distillation (for liquids), column chromatography, or crystallization (Table I).

2-[(Methoxymethyl)carbonyl]furan (12): obtained in 60% yield; bp 66–68 °C (0.01 mm); IR (neat) 1705 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.53 (s, 3 H, OCH_3), 4.58 [s, 2 H, $C(=O)CH_2$], 6.4 (dd, 1 H, furan 3-H), 7.15 (d, 1 H, furan 2-H), 7.50 (d, 1 H, furan 4-H). Anal. Calcd for $C_7H_8O_3$: C, 60.00; H, 5.71. Found: C, 59.54; H, 5.83.

2-[(Methoxymethyl)carbonyl]thiophene (13): obtained in 54% yield; bp 59–62 °C (0.01 mm); IR (neat) 1705 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.53 (s, 3 H, OCH_3), 4.58 [s, 2 H, $C(=O)CH_2$], 7.11–7.30 (m, 1 H, thiophene), 7.70–8.0 (m, 2 H, thiophene). Anal. Calcd for $C_7H_8O_2S$: C, 53.84; H, 5.12; S, 20.51. Found: C, 53.70; H, 5.02; S 20.38.

2-[(Methoxymethyl)carbonyl]pyridine (8). Boron trifluoride etherate (17.00 g, 0.12 mol) was dissolved in dry dichloromethane (500 mL), and iodosobenzene (9.68 g, 0.044 mol) was added. The mixture was cooled to −70 °C and then silyl enol ether **6** (7.72 g, 0.040 mol) was added. Finally, methanol (10 mL) was added. The reaction mixture was stirred at −70 °C for 1 h, and then the temperature was slowly raised to room temperature. Stirring was continued for another 30 min. Water (50 mL) was added, and the mixture was neutralized with a saturated solution of sodium bicarbonate and then transferred to a separatory funnel. The aqueous layer was extracted with dichloromethane (4 × 50 mL). The organic phases were combined, dried with magnesium sulfate, and concentrated in vacuo to yield the crude product which did not show any starting material (by TLC and NMR). Distillation of crude product afforded pure **8**: 4.24 g (70%); bp 82–83 °C (0.05 mm) (some of the product decomposed during distillation; higher temperatures for distillation are not recommended); IR (neat) 1720 cm^{-1} (C=O str); ^1H NMR ($CDCl_3$) δ 3.53 (s, 3 H, OCH_3), 5.02 [s, 3 H, $C(=O)CH_2$) 7.30–8.05 (m, 3 H, pyridine), 8.62–8.80 (m, 1 H, pyridine); MS, m/z 151 ($M^{\cdot+}$, 10), 136 (100). Anal. Calcd for $C_8H_9NO_2$: C, 63.58; H, 5.96; N, 9.27. Found: C, 63.29; H, 6.10; N, 9.11.

2,6-Bis[(methoxymethyl)carbonyl]pyridine (9). Silyl enol ether **7** (6.14 g, 0.020 mol) was treated with iodosobenzene (8.80 g, 0.040 mol), boron trifluoride etherate (11.36 g, 0.080 mol), and 10 mL of methanol in 500 mL of dry dichloromethane. To the crude mixture (obtained as described in case of **8**) was added hexane (50 mL), and the resulting mixture was allowed to stand for a few minutes, filtered, and cooled slowly to about 10 °C. After 30 min, colorless crystalline product [2.67 g (60%); mp 100–101 °C] was collected by filtration and drying. Recrystallization from hexane gave an analytical sample, mp 101–102 °C. Filtrates gave more of the product: total yield 3.16 g (71%); IR (Nujol) 1720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.55 (s, 6 H, 2 OCH_3), 5.05 (s, 4 H, 2 $CH_3OCH_2C{=}O$), 8.05–8.40 (m, 3 H, pyridine); MS, m/z 223 ($M^{\cdot+}$, 10), 208 ($M^{\cdot+}$ − Me, 100), 192 (8), 176 (18), 134 (27), 105 (20).

α-Ethoxyacetophenone (18). This compound was obtained by the treatment of acetophenone silyl enol ether **2a** (3.84 g, 0.020 mol) with iodosobenzene and ethanol under the conditions described for methoxylation. Distillation of the crude product gave

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(17) Griesbaum, K.; Lie, G. O.; Keul, H. *J. Org. Chem.* **1984**, *49*, 679.
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(19) Addition of water was essential at this stage because the dimethyl acetal of α-methoxy ketone was obtained in some cases when the mixture was directly neutralized with $NaHCO_3$.

pure **18**: 2.62 g (80%); bp 123–125 °C (10 mm) [lit.[1] bp 125–127 °C (11 mm)]; ^{1}H NMR ($CDCl_3$) δ 1.22 (t, 3 H, CH_2CH_3), 3.54 (q, 2 H, OCH_2) 4.64 (s, 2 H, $COCH_2$), 7.20–7.89 (m, 5 H).

α-Isopropoxyacetophenone (19). Use of isopropyl alcohol instead of ethanol in the last experiment yielded **19**: 1.49 g (42%); bp 87–88 °C (2 mm) [lit.[1] bp 87 °C (2 mm)]; ^{1}H NMR ($CDCl_3$) δ 1.20 [d, 6 H, $CH(CH_3)_2$], 3.62 (m, 1 H, $CH(CH_3)_2$], 4.61 (s, 2 H, $COCH_2$), 7.12–7.85 (m, 5 H).

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Notes

Stereoselection in the Hypervalent Iodine Oxidation of Chromium Tricarbonyl Complexes of Benzocyclanones

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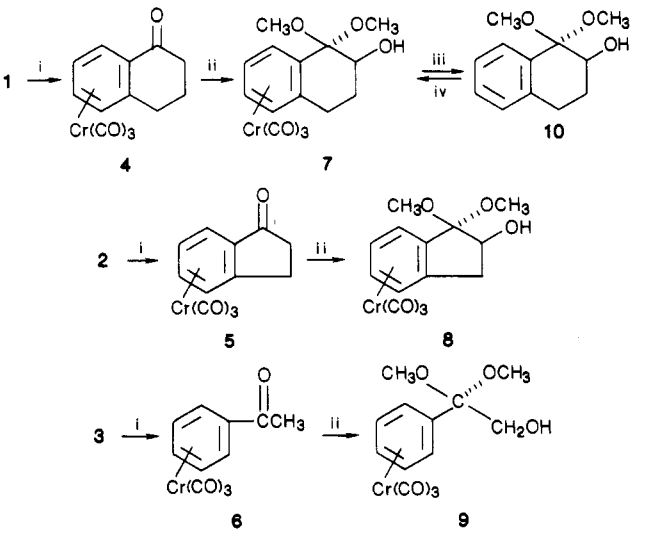
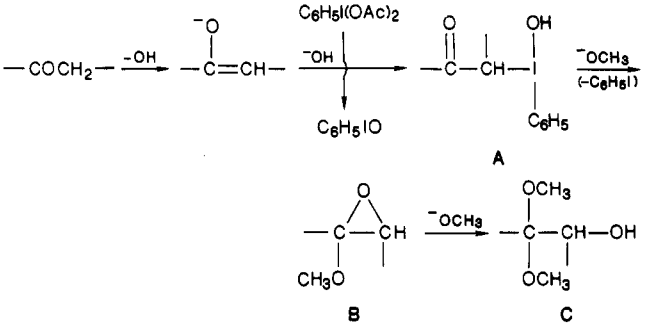
1-Tetralone (**1**) and 1-indanone (**2**) are achiral molecules that become chiral upon complexation with $Cr(CO)_3$: i.e., **1** → (η^6-1-tetralone)tricarbonylchromium(0) (**4**)[1] and **2** → (η^6-1-indanone)tricarbonylchromium(0) (**5**).[1a,b] **1** and **2** may be regarded more precisely as (pro)[1]-chiral molecules.[2] The carbon atom at C2 is prostereogenic in the sense that introduction of a substituent by replacement of a hydrogen atom may yield proximate or distal orientations of that substituent with respect to the $Cr(CO)_3$ tripod. Furthermore, if the steric size of the group introduced at C2 is large, one might expect a high degree of stereoselection.[3] Since **1** and **2** have been resolved and the absolute configurations of the enantiomers are known,[1] stereospecific functionalization at C2 must yield a single diastereomer of known absolute configuration at C2, and subsequent disengagement of the ligand must likewise yield an enantiomer of known absolute configuration. α-Hydroxy dimethylacetal formation in the hyperiodination procedure for ketones[4] involves the intermediary introduction of the large $-I(OH)C_6H_5$ group α to the carbonyl group. This circumstance renders the reaction highly stereospecific.[5] The operation of a steric effect between $-I(OH)C_6H_5$ and the $Cr(CO)_3$ tripod was probed in the cases of **4** → **7**, **5** → **8**, and **6** → **9** with the expectation of realizing all the points of stereochemistry mentioned above.

Scheme I[a]



[a] Key: (i) $Cr(CO)_6$/diglyme; (ii) $C_6H_5I(OAc)_2$, KOH/MeOH; (iii) sunlight/air; (iv) $Cr(CO)_3(CH_3CN)_3$/dioxane.

Scheme II



The observed stereochemical course of **4** → **7** [OH proximate to $Cr(CO)_3$] can be rationized on the basis of the general mechanism that we determined for the hyperiodination of ketones to yield α-hydroxy dimethyl acetals.[4e,5]

Formation of **A** in the case of **4** or **5** must occur with addition of C_6H_5IO from the opposite face relative to the $Cr(CO)_3$ group because of a destabilizing steric interaction were these groups mutually proximate. Formation of **B** occurs with inversion of configuration at C2, thus placing the ring oxygen on the same face as the $Cr(CO)_3$.[5] The oxirane oxygen atom becomes the hydroxyl oxygen with retention of configuration at C2 in the displacement reaction **B** → **C** (Scheme II).

The molecular structure **7** as determined by X-ray diffraction is presented in Figure 1.[6] The stereochemical

(1) (a) A preliminary communication of this work was reported: Moriarty, R. M.; Engerer, S. C.; Prakash, O.; Prakash, I.; Gill, U.S.; Freeman, W. A. *J. Chem. Soc., Chem. Commun.* **1985**, 1715. (b) Jaouen, G.; Meyer, A. *J. Am. Chem. Soc.* **1975**, *97*, 4667.

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