Hypervalent Iodine Oxidation of Chromium Tricarbonyl Complexes of Benzocycloalkanones and Acetophenone

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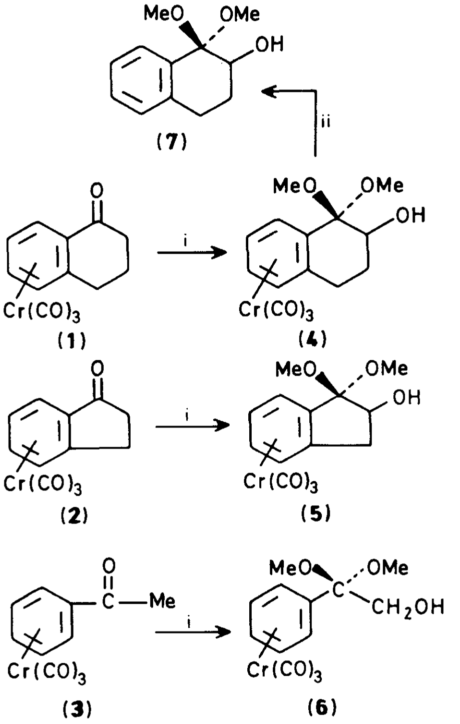
Hypervalent iodine oxidation of the title compounds occurs stereoselectively and regiospecifically to yield the Cr(CO)$_3$ complex of the derived α-hydroxy dimethyl acetal.

The oxidizing agent PhI(OAc)$_2$–KOH–MeOH converts α-methylene carbonyl compounds into the corresponding α-hydroxy dimethyl acetal derivatives with a high degree of regioselectivity and stereoselectivity.[1] It appeared of interest to apply this reaction to η^6-benzocycloalkanone and acetophenone tricarbonylchromium compounds in order (a) to test the compatibility of the easily oxidized Cr^0(CO)$_3$ group with the oxidizing agent[2] and (b) to use the steric effect of the Cr(CO)$_3$ tripod to achieve diastereoselectivity in the reaction.[3] 1-Tetralone, indan-1-one, and acetophenone were converted into their η^6-tricarbonylchromium(0) complexes (**1**), (**2**), and (**3**), respectively, by treatment with Cr(CO)$_6$ in diglyme, and these complexes were converted in each case by PhI(OAc)$_2$–KOH–MeOH into the single diastereoisomers (**4**), (**5**), and (**6**), respectively (Scheme 1).† The stereochemistry of complex (**4**) was established by *X*-ray crystallography (Figure 1).‡ The C-2 hydroxy group is found to be proximate to the Cr(CO)$_3$ group.



Scheme 1. *Reagents/conditions:* i, PhI(OAc)$_2$, KOH, MeOH; ii, sunlight, air.

The overall stereochemical course may be understood in terms of initial addition of PhIX$_2$ to the enolate anion at a position distal to Cr(CO)$_3$§ to yield (A) (Scheme 2). Attack of

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† The n.m.r. spectra of the crude products showed only two OMe resonances in each case, *e.g.* at δ 3.20 and 3.46 for (**4**). The compounds were purified by recrystallization and the isolated yields were as follows: (**4**), 40%, m.p. 176—179 °C; (**5**), 60%, m.p. 143—144 °C; (**6**), 40%, m.p. 96—98 °C. All compounds gave satisfactory microanalyses.

‡ *Crystal data for* (**4**): triclinic, space group $P\bar{1}$, a = 7.527(2), b = 9.250(3), c = 11.945(5) Å, α = 106.60(3), β = 103.87(3), γ = 103.65(2)°, U = 731.2(4) Å^3, Z = 2, D_c = 1.564 g cm^{-3}. Data were collected on a Picker FACS-1 automatic diffractometer modified by a Krisel Control update package. A total of 1694 unique reflections with $F > 3.0\sigma(F)$ in the range 2.0 $< 2\theta <$ 45.0° were used in the structure analysis. The data were corrected for absorption and secondary extinction. The structure was solved by direct methods and refined to R = 0.0601, R_w = 0.0488 using 204 variable parameters (ACSHEL-X, G. Sheldrick, Programs for Crystal Structure Determination, Cambridge, 1975). The phenyl carbon atoms were refined as part of a rigid hexagon. All hydrogen atoms were placed at calculated positions (C–H = 1.08 Å) except the hydroxy hydrogen atom which was located in a difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were divided into three groups and refined with three isotropic thermal parameters. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

§ The product of reaction of PhI(OAc)$_2$ with KOH–MeOH is ultimately (PhIO)$_n$ but the active reagent in the present case may be PhI(OH)OMe or PhI(OMe)$_2$.

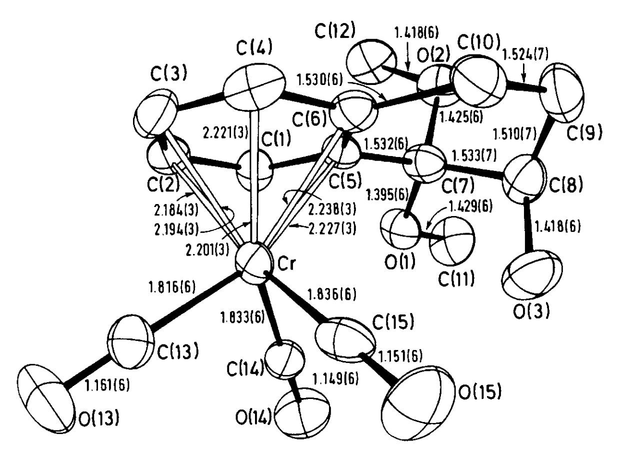
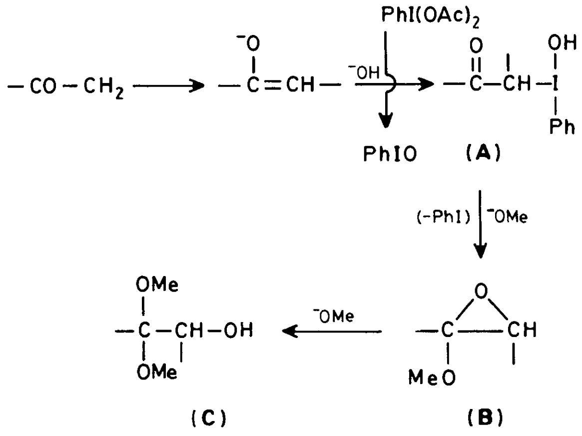
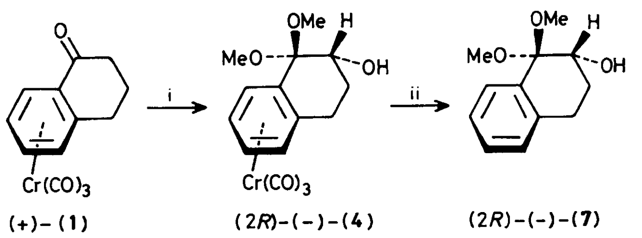


Figure 1. Perspective view (ORTEP) of (**4**) with bond distances. H atoms are omitted. The $\mathrm{Cr(CO)_3}$ tripod does not eclipse the arene ring carbon atoms. Sighting down the Cr–Z axis (where Z is the centroid of the benzene ring) the torsional angles are −17.6 (3), −17.0(3), and −17.7(3)°.



Scheme 2

MeO$^-$ at the carbonyl group and subsequent intramolecular reductive elimination of PhI, (A) → (B), occurs with inversion of configuration, thus placing the epoxide ring in (B) proximate to $\mathrm{Cr(CO)_3}$. Finally, the conversion (B) → (C) fixes the stereochemistry of the hydroxy group as proximate to $\mathrm{Cr(CO)_3}$.



Scheme 3. *Reagents/conditions:* i, $\mathrm{Cr(CO)_6}$, diglyme; ii, sunlight, air.

As a further test of the selectivity of hypervalent iodine as an oxidant in organometallic chemistry, α-hydroxy dimethyl acetal formation was carried out in the optically active series. The enantiomer of (**1**) with $[\alpha]_D^{23}$ +810° (*c*, 0.35, $\mathrm{CHCl_3}$)[4] was converted into (2*R*)-(**4**), $[\alpha]_D^{24}$ −44° (*c*, 0.058, $\mathrm{CHCl_3}$), from which the free ligand was obtained by using sunlight in air[5] to yield (2*R*)-(**7**), $[\alpha]_D^{24}$ −40° (*c*, 0.096, $\mathrm{CHCl_3}$) (Scheme 3).¶

The achiral 1-tetralone becomes chiral upon complexation and from a knowledge of the absolute configuration of the complex (+)-(**1**) the absolute configuration at C-2 as (2*R*) in (−)-(**4**) and (2*R*) in (−)-(**7**) is established.

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References

1 For an example see R. M. Moriarty, O. Prakash, and W. A. Freeman, *J. Chem. Soc., Chem. Commun.*, 1984, 927.

2 Iodosylbenzene has been used for the oxidation of transition metal carbenoid complexes. The ligand is dissociated by oxidation at the metal centre; C. M. Lukehart and J. V. Zeile, *J. Organomet. Chem.*, 1975, **97**, 421.

3 For a recent discussion of steric effects in addition reactions see, *inter alia*, W. S. Trahanovsky and R. J. Card, *J. Am. Chem. Soc.*, 1972, **94**, 2898; G. Jaouen, S. Top, A. Laconi, D. Couturier, and J. Brocard, *ibid.*, 1984, **106**, 2207.

4 G. Jaouen and A. Meyer, *J. Am. Chem. Soc.*, 1975, **97**, 4667.

5 G. Jaouen and R. Dabard, *Tetrahedron Lett.*, 1971, 1015.

¶ Rotations were measured on a Perkin-Elmer MC-241 polarimeter. Only one enantiomer was present by n.m.r. measurement using $\mathrm{Eu(hfc)_3}$ [hfc = 3-(heptafluoropropylhydroxymethylene)-(+)-camphorato]. (H. L. Goering, J. N. Eikenberry, and G. S. Koermer, *J. Am. Chem. Soc.*, 1971, **93**, 5913).