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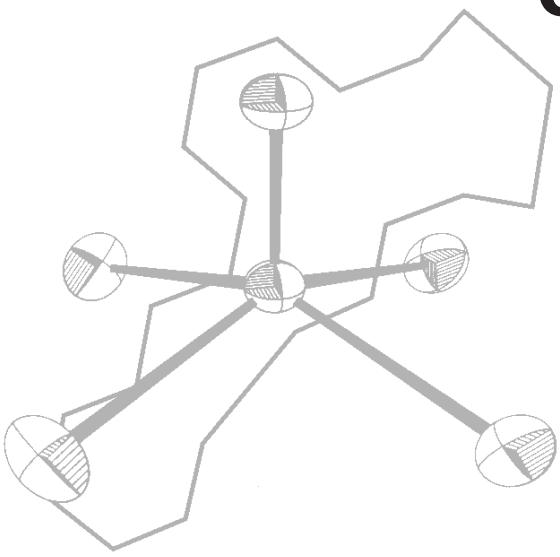

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Towards the Diastereoselective Functionalization of Non-Racemic Acetal Derivatives of η^6-Arylcarbonyl Complexes of Tricarbonylchromium

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(*S*)-Butane-1,2,4-triol (2) has been investigated as a potential chiral auxiliary for the formation of non-racemic acetals derived from η^6-arylcarbonyl complexes of tricarbonylchromium. Predominantly the *cis* dioxan (5) was formed from benzaldehyde, leading to preparation of the η^6-$Cr(CO)_3$ complex (16), and of the derived complexes (23) and (24). Lithiation–electrophile quenching of these complexes gave a mixture of products arising from *ortho* and benzylic functionalization. Reaction of acetophenone, or of the η^6-$Cr(CO)_3$ complexes (45) or (46), with either the triol (2) or its tris(silyl) ether (15) under conditions of kinetic or thermodynamic control gave an inseparable mixture of acetals.

Introduction

As part of a continuing program directed at the synthesis and reactions of (η^6-arene)tricarbonylchromium complexes[1] we have been interested in utilizing chiral auxiliaries which confer diastereotopicity on the pairs of *ortho* (or *meta*) hydrogen atoms of the arene. The consequence of such inequivalence can be utilized in reactivity discrimination between such pairs in the complex; the resulting ability to functionalize one *ortho* site selectively has been applied to the synthesis of chiral metal-free organic molecules.[2] One method for exposing the latent asymmetry relies on the development of diastereoisomeric transition states during the approach of a chiral non-racemic base to the *ortho* hydrogen atoms, in an overall deprotonation–electrophile quenching sequence.[3,4] An alternative method relies on the attachment of a non-racemic auxiliary to the arene ring in order to achieve the desired discrimination. Kagan has recently disclosed[5] the application of a chiral non-racemic auxiliary derived from (*S*)-malic acid (1) to the diastereoselective functionalization of ferrocenecarbaldehyde. We report here some results that aimed at extending this work to acetals derived from (*S*)-butane-1,2,4-triol (2) and the η^6-tricarbonylchromium complexes of benzaldehyde or acetophenone.

Results and Discussion

Aryl carbonyl compounds themselves are not sufficiently electron-rich to form η^6-tricarbonylchromium complexes in acceptable yield. However, a cyclic acetal derivative serves the dual purpose of not only permitting complexation in high yield but also of providing a site for inclusion of a stereogenic centre (either in the acetal ring, or subtended from it). (*S*)-Butane-1,2,4-triol was selected for the preparation of chiral non-racemic acetals derived from benzaldehyde and acetophenone; this chiral auxiliary is easily hydrolysed, enabling the facile synthesis of either enantiomerically enriched or pure *ortho* disubstituted benzaldehyde and acetophenone tricarbonylchromium complexes. Moreover, the hydroxy group at C 2 can provide a locus for chelation interaction during the proposed deprotonation–electrophile quenching sequences, which may be important for optimum diastereoselection. Initially, synthesis of (*S*)-butane-1,2,4-triol (2) was attempted from commercially available (*S*)-malic acid (1) via dimethyl (*S*)-2-hydroxybutanedioate (3). The diester (3) was made (88%) by standing a solution of (1) in dry methanol, with hydrochloric acid as a catalyst, at room temperature for 5 days.[6] Attempted reduction of the diester to (*S*)-butane-1,2,4-triol (2) using sodium bis(2-methoxyethoxy)aluminium hydride in dry tetrahydrofuran at room temperature for 4 days was unsuccessful, while treatment with sodium borohydride[7] gave a mixture of products, which possibly included a monomethyl ester and a lactone. In contrast, direct reduction of the diacid (1) with borane–dimethyl sulfide[8] in the presence of trimethyl borate gave the triol (2) in 87% yield.

The synthesis of (2*S*,4*S*)-2-phenyl-1,3-dioxan-4-methanol (5) was attempted from benzaldehyde and the triol (2) with *p*-toluenesulfonic acid as the catalyst, by refluxing in toluene in a Soxhlet extractor containing 4 Å molecular sieves.[9] However, none of the desired product formed. Since transacetaliza-

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tion is often successful when the direct method fails, (dimethoxymethyl)benzene (4) (from benzaldehyde and methanol with tungstosilicic acid catalyst,[10] 62%) was refluxed with the triol (2) in hexanes under a Dean–Stark separator, with *p*-TsOH as the catalyst.[11] However, the dimethoxy acetal (4) hydrolysed to benzaldehyde (due presumably to the water of hydration in *p*-TsOH), and gave none of the desired product. In contrast, pyridinium *p*-toluenesulfonate, which is not hydrated, was an efficient catalyst. Although Kagan *et al.*[5] isolated only the *cis* dioxan (5), six acetals (the *cis* and *trans* isomers of five-, six- and seven-membered rings) are possible from this reaction and four were in fact formed. The signal due the benzylic hydrogen in the ^{1}H n.m.r. spectrum is unique for each acetal (Table 1); the major isomer (5) shows this signal at 5·48 ppm.[7,12,13] This structure was consistent with the other ^{1}H n.m.r. signals and coupling constants, as determined from decoupling experiments. Two less intense peaks, at 5·75 and 5·88 ppm, were assigned to (2*R*,4*S*)-2-phenyl-1,3-dioxolan-4-ethanol (6) and (2*S*,4*S*)-2-phenyl-1,3-dioxolan-4-ethanol (7), respectively, since the signal due to H 2 is downfield in a *trans* isomer compared with the *cis* isomer.[14] The mixture of acetals was also analysed by g.c.–m.s. As expected,[15] the retention time (Table 1) was shorter for the *cis* isomer of each pair and each pair of diastereoisomers had nearly identical but characteristic mass spectra (Experimental), which were different from those of the other pairs. The minimum conformational energy for each isomer was computed by using Macromodel (MM2, Monte Carlo; Table 1) in an attempt to predict their relative thermodynamic stabilities. The two dioxolans (6) and (7) had the lowest computed energies, but they were not the major products found experimentally, although the transacetalization reaction had been carried out under conditions of apparent thermodynamic control.

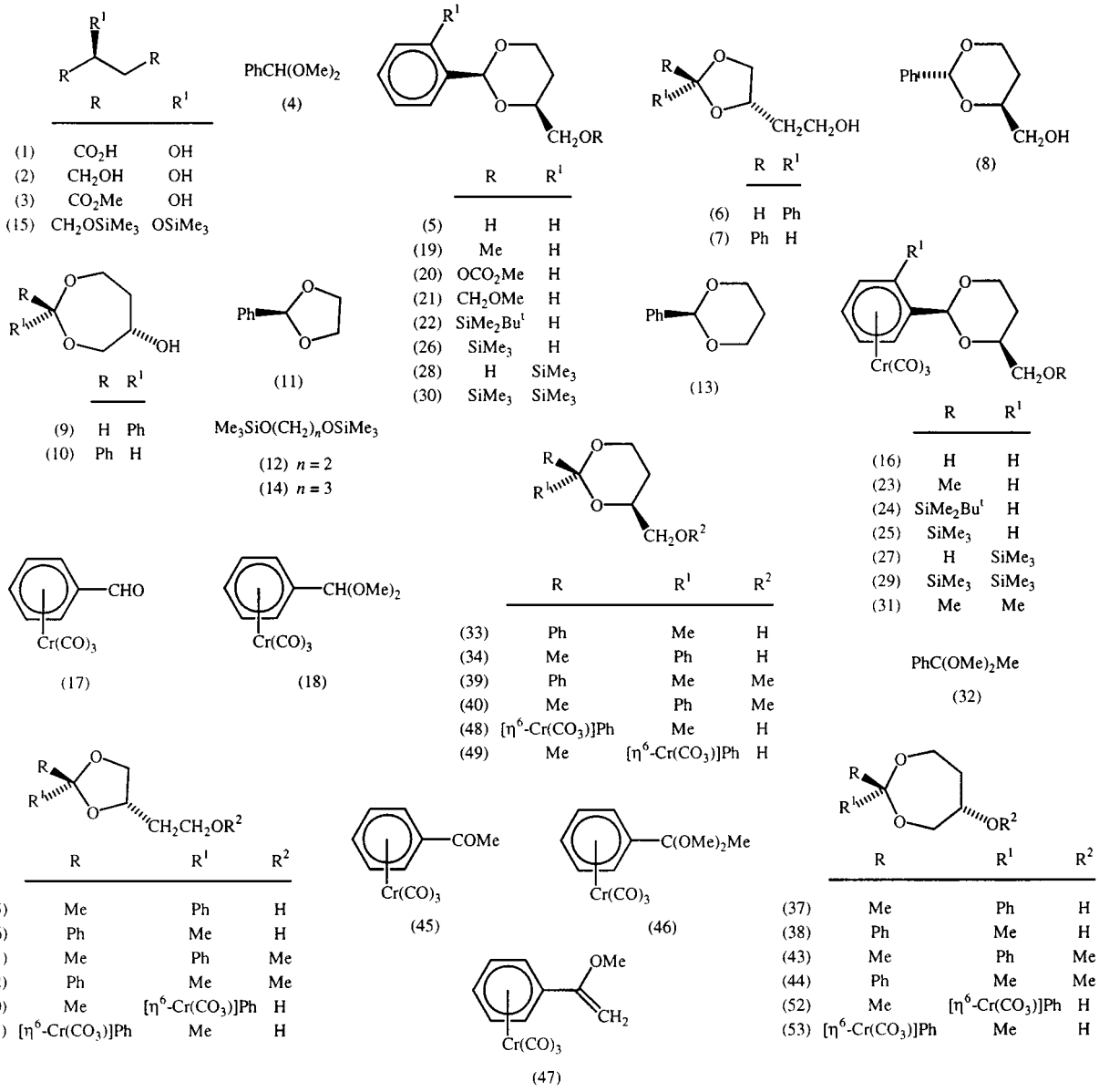


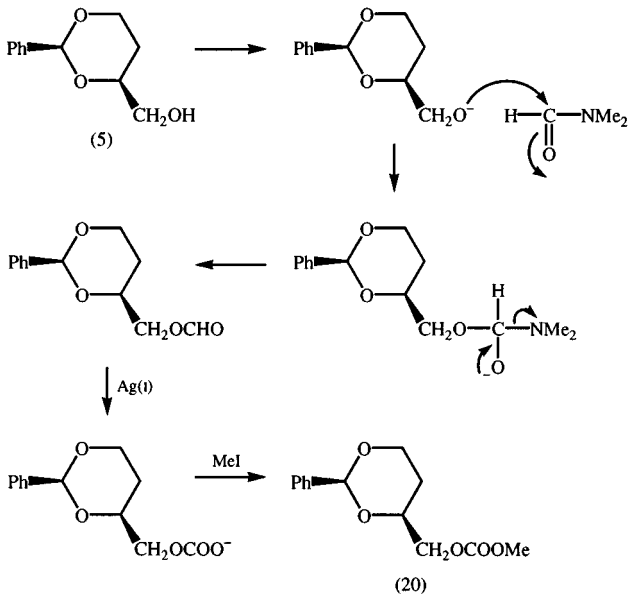
Table 1. Data for the isomeric acetals (5)–(10)

Compound	δ H2 (ppm)	R_t (min)	Ratio (%)	Energy (kJ mol^{-1})
(5)	5·48	20·33	82	−27·98
(8)	—	21·13	2	−25·85
(6)	5·75	21·91	9	−37·67
(7)	5·88	22·48	7	−38·38
(9)	—	—	—	−1·50
(10)	—	—	—	−0·87

Acetals can also be made under conditions of kinetic control, at −78°C, from an aldehyde or a ketone and a 1,2-bis(trimethylsilyl) ether by using trimethylsilyl trifluoromethanesulfonate as the catalyst.[16] In model reactions, benzaldehyde gave 2-phenyl-1,3-dioxolan (11) (54%) under these conditions by reaction with the bis(silyloxy) derivative (12) of ethane-1,2-diol, and also the six-membered ring analogue 2-phenyl-1,3-dioxan (13) (53%) from 2,2,8,8-tetramethyl-3,7-dioxa-2,8-disilanonane (14). Therefore, the tris(silyl ether) (*S*)-2,2,9,9-tetramethyl-5-[(trimethylsilyl)oxy]-3,8-dioxa-2,9-disiladecane (15) was made (100%) from the chiral non-racemic triol (2) by using chlorotrimethylsilane and triethylamine,[17] and was then reacted with benzaldehyde and trimethylsilyl trifluoromethanesulfonate, initially at −78°C (slow) and then at −42°C for 4 h. The side-chain trimethylsilyl group hydrolysed during workup to give (80%) a mixture (^{1}H n.m.r.) of (5) (98%), (6) (1%) and (7) (1%). This method was also tried with the dimethyl acetal (4) instead of benzaldehyde at −42°C, but the crude yield (21%) was much lower and the minor components were more significant [(5), 80%; (6), 12%; (7), 8%]. Attempted equilibration by refluxing this mixture overnight in 1,2-dichloroethane with a catalytic amount of pyridinium *p*-toluenesulfonate was unsuccessful, the ratios being unchanged.

Tricarbonyl[(2*S*,4*S*)-2-(η^6-phenyl)-1,3-dioxan-4-methanol]chromium (16) was then synthesized, both from [(1,2,3,4,5,6-η)-benzaldehyde]tricarbonylchromium (17), and from tricarbonyl[(1,2,3,4,5,6-η)-(dimethoxymethyl)benzene]chromium (18) prepared by refluxing the dimethyl acetal (4) with $Cr(CO)_6$ in Bu_2O/tetrahydrofuran (9 : 1).[18] The aldehyde complex (17) was stirred with the tris(silyl ether) (15) and trimethylsilyl trifluoromethanesulfonate as catalyst in dry CH_2C1_2 at −42°C and then at −23°C to give (16) in 51% yield. Similar reaction of the acetal complex (18) gave (16) in lower yield (32%), the major product being the η^6-$Cr(CO)_3$ complex of the major dioxan component (5) obtained from reaction of the non-complexed arene.

Protection of the hydroxy group in the 1,3-dioxan (5) was then attempted by using several methods, but with limited success (difficulties in methylating the hydroxy group of dimethyl (*S*)-2-hydroxybutanedioate (3) with a base and MeI have been reported recently;[19] only a low yield of the ether was obtained, together with a large amount of olefinic esters). Unexpectedly, treatment of (5) with BuLi in dry tetrahydrofuran at −78°C and quenching with MeI returned starting material. Powdered KOH and MeI in dry dimethyl sulfoxide[20] gave (19) in only 6% yield, which was increased (32%) by using dimethyl sulfate and NaOH in Et_2O/H_2O in the presence of tetrabutylammonium iodide,[21] and increased again (47%) by the use of sodium hydride–imidazole and then MeI. The ^{1}H n.m.r. spectrum of the product, (2*S*,4*S*)-4-(methoxymethyl)-2-phenyl-1,3-dioxan (19), from the latter reaction showed only one signal due to a benzylic hydrogen atom, and g.c.–m.s. analysis confirmed that the ether was of higher purity than the precursor alcohol, the only contaminant being a trace (*c.* 1%) of a dioxolan. The use of potassium hydride as the base with MeI increased the yield further (57%). Interestingly, the use of silver(I) oxide and MeI in *N*,*N*-dimethylformamide[22] afforded only the methyl carbonate (20) (37%). The molecular formula of (20) was confirmed by accurate measurement of the molecular ion in the mass spectrum, and the infrared spectrum included intense absorptions at 1749 and 1273 cm^{-1} (cf. dimethyl carbonate, ν_{max} 1750, 1270 cm^{-1}). The signal due to OCH_3 in the ^{1}H n.m.r. spectrum moved from 3·41 for (19) to 3·79 ppm for (20). A possible mechanism for the formation of (20) is outlined in Scheme 1.



Scheme 1

In order to provide an alternative side chain having either a directing chelating or steric effect during the proposed complexation–deprotonation–electrophile quenching sequence, the preparation of (2*S*,4*S*)-4-(methoxymethoxymethyl)-2-phenyl-1,3-dioxan (21) from alcohol (5) was investigated, but again only very low yields were obtained. Thus, treatment of (5) with *N*-ethyldiisopropylamine and bromomethyl methyl ether gave (21) (15%), benzaldehyde (30%) and starting material (23%). The use of dried K_2CO_3 and a catalytic amount of 18-crown-6[23] with $BrCH_2OCH_3$ produced mainly benzaldehyde, as did stirring overnight in dimethoxymethane with a catalytic

amount of *p*-TsOH. The synthesis of (2*S*,4*S*)-4-[(t-butyldimethylsilyl)oxy]methyl-2-phenyl-1,3-dioxan (22) was more successful, treatment of the alcohol (5) with 1,8-diazabicyclo[5.4.0]undec-7-ene and Bu^tMe_2SiCl[24] giving (22) in 45% yield.

The tricarbonylchromium complexes of the alcohol (5), of the methyl ether (19) and of the silyl ether (22) were made by the usual thermally promoted method[18] to give (16), tricarbonyl[(2*S*,4*S*)-4-(methoxymethyl)-2-(η^6-phenyl)-1,3-dioxan]chromium (23), and tricarbonyl-{(2*S*,4*S*)-4-[(t-butyldimethylsilyl)oxy]methyl-2-(η^6-phenyl)-1,3-dioxan}chromium (24), respectively. Purification of these complexes was difficult because the R_F value of each was similar to that of the parent ligand, and flash chromatography required the complexes to be in solution (Et_2O or CH_2Cl_2) where they were somewhat unstable (even under N_2 pressure and in the absence of light). Each η^6-$Cr(CO)_3$ complex was isolated as a yellow oil. Although (16) solidified after 1 month, and could be recrystallized by vapour diffusion using hexanes–CH_2Cl_2, efforts to obtain a single crystal for X-ray crystallographic analysis were frustrated by its reversion to an oil on attempted drying of the crystals by means of an oil pump.

With the tricarbonylchromium complexes of the *cis* 1,3-dioxan (5) and some of its derivatives in hand, some lithiation and electrophile quenching reactions were investigated. Thus, (16) was treated with BuLi or with Bu^tLi in tetrahydrofuran at −78°C, and the reaction mixture quenched with D_2O. The reaction mixture with BuLi remained yellow during the entire process, but when Bu^tLi was used the mixture turned brown before workup and the crude product was therefore decomplexed by exposing the solution to air and sunlight. In each case a large O–H peak was present in the infrared spectrum and no O–D peak (2400–2600 cm^{-1}) was detected; therefore the deuterium was bound to carbon. The decomplexed product from lithiation with Bu^tLi contained (^1H n.m.r., mass spectrometry) 0·35 benzylic deuterium atoms and 0·78 aromatic deuterium atoms per molecule. The mass spectrum also included a weak signal at *m/z* 250, corresponding to the molecular ion from addition of t-butyl carbanion to the complex. When BuLi was used as the base, there were (^1H n.m.r., mass spectrometry) 0·13 benzylic deuterium atoms and 0·82 *ortho* aromatic deuterium atoms incorporated per molecule (Table 2). There was no signal at *m/z* 250 due to the product resulting from nucleophilic attack of t-butyl carbanion.

Table 2. Deuterium incorporation (%) in (5) (with tetrahydrofuran as solvent)

Deuterium position	Bu^tLi	BuLi
No D	0	12
Benzylic D	22	6
1 Aromatic D	39	62
Benzylic and 1 aromatic D	5	5
2 Aromatic D	26	13
Benzylic and 2 aromatic D	8	2

These results indicate that BuLi is a more selective base than Bu^tLi for deprotonation of (16) because it removes fewer benzylic hydrogen atoms, it gives a greater proportion of the product from deprotonation of just one aromatic site, and there is no evidence that it behaves as a nucleophile. The BuLi/D_2O experiments were repeated in diethyl ether as the solvent at −42°C. The stable yellow complex obtained after workup contained (^1H n.m.r., mass spectrometry) 0·1 deuterium atoms in the benzylic position and 0·4 in the *ortho* aromatic sites. Thus, tetrahydrofuran is preferred to Et_2O as solvent during the deprotonation reaction as judged from the use of deuterium as the electrophile.

When Me_3SiCl was used as electrophile after deprotonation with BuLi at −78°C both tetrahydrofuran and diethyl ether as solvent gave a brown oil. Flash chromatography within 10 min of workup produced the largest amounts of the intact product complex, which was relatively stable. If the crude reaction mixture was allowed to stand under nitrogen for 1 h, a large amount of decomplexation took place. Chromatography of the crude product from reaction in tetrahydrofuran gave three fractions. The two smaller fractions were identified as a mixture (15%) of the silyl ether complex (25) and its free ligand (26) and a mixture (10%) of the 2-trimethylsilyl complex (27) and its free ligand (28). Products (25)/(26) showed no change in the aromatic region of the ^1H n.m.r. spectrum from the starting material (16). The presence of a singlet at 0–0·5 ppm in the ^1H n.m.r. spectrum and the characteristic absorbances in the infrared spectrum near 1250 and 840 cm^{-1} confirmed the presence of a trimethylsilyl group. The aromatic region of the ^1H n.m.r. spectrum of the arylsilanes (27)/(28) was significantly different from that of the starting material, which suggested that a trimethylsilyl group was attached to the aromatic ring at an *ortho* site [note that structures (27), (29), and (31) do not represent the absolute configuration of electrophile incorporation]. Two $SiMe_3$ singlets with similar integrated areas (0·35, 0·38 ppm) may represent diastereoisomeric *ortho* products. Alternatively, they may be due to the complexed and uncomplexed products (27) and (28). The major fraction (40%) was also a mixture of complexed and uncomplexed acetals, a high-resolution mass spectrum confirming the incorporation of both one $SiMe_3$ group (*m/z* 402) and two $SiMe_3$ groups (*m/z* 474). The ^1H n.m.r. spectrum ($CDCl_3$ or C_6D_6) was difficult to assign due to the presence of both complexed and uncomplexed products, and due to overlap of the signals due to benzylic hydrogens with those of aromatic hydrogens in an η^6-$Cr(CO)_3$ complex. Decoordination of the tricarbonylchromium group by exposure of a solution of this fraction to air and sunlight simplified the spectrum (and also partially hydrolysed the O–$SiMe_3$ group). The original major fraction was then assigned as containing mainly the complex (29) and its free

ligand (30), together with a small amount of the arylsilanes (27)/(28) which resulted from partial hydrolysis during or after the chromatographic separation.

When this reaction was repeated in diethyl ether, one major fraction was isolated after immediate flash chromatography. A high-resolution mass spectrum (c.i., NH_3) of the decomplexed fraction identified products incorporating both one and two $SiMe_3$ groups (MH^+ 267 and 339, respectively). G.c.–m.s. showed two arylsilane products (27) and (28); (30) was also shown to contain a silyl ether. As an aid to determine the preferred direction of diastereoselectivity, the two proposed lithiated intermediates were modelled (Cerius, Universal Force Field). The relative energy minima indicate that abstraction of the *pro-S* hydrogen is preferred over abstraction of the *pro-R* hydrogen by 27·6 kJ mol^{-1}. Kagan *et al.*[5] demonstrated exclusive *pro-S* hydrogen removal from a ferrocene analogue experimentally, supporting the relative total energies of the computed lithiated intermediates in the present case.

Methylation of the complexed aryllithium would allow the direction and extent of diastereoselectivity of *ortho* lithiation to be determined experimentally. Thus, hydrolysis of the resulting acetal would give the η^6-$Cr(CO)_3$ complex(es) of 2-methylbenzaldehyde, of known absolute configuration.[25–27] Therefore, iodomethane was used as the electrophile (BuLi or Bu^{t}Li, −78°C; or −78 to 0 to −78°C then MeI; or transmetallation to an arylcopper then MeI). However, only the starting complex and its parent ligand were recovered. Methyl triflate as the electrophile (BuLi, Et_2O, −78°C) gave the aldehyde (17) (26%; via attack of the hard methyl cation on an acetal oxygen) and the *O*-methyl ether (23) (48%). Warming to either −23 or 0°C before the addition of methyl triflate at −78°C did give a product of aromatic methylation, decomplexed (31), but only in very low yield (3 and 4% respectively) and contaminated by decomplexed (23) (32 and 18% respectively). These results indicate that, although excess of BuLi had been used, the alcohol complex (16) is not a suitable substrate for arene lithiation. However, treatment of the methyl ether derivative (23) with BuLi at −42°C and then with D_2O did not result in deuteration, and use of Me_3SiCl as the electrophile at −78°C resulted only in recovery of the starting complex (13%) together with its parent ligand (26%). Although the complexed t-butyldimethylsilyl derivative (24) gave better results (BuLi, −42°C; D_2O), the crude yellow oil incorporating (^{1}H n.m.r., mass spectrometry) 0·5 deuterium atoms per molecule and only at an *ortho* site, this is still not sufficient for use of this method for further syntheses. Overall, this set of results shows not only that the optimum conditions for arene lithiation/electrophile quenching are unique for each individual tricarbonylchromium complex, but also that the chemical yields are too low and any diastereoselection is therefore of little value.

One problem associated with the lithiation reactions described above arises from the stabilizing effect of the tricarbonylchromium moiety on a benzylic anion.[28–34] Therefore, preparation of the acetophenone analogue of (16) was investigated. In contrast to the result obtained from benzaldehyde, refluxing (1,1-dimethoxyethyl)benzene (32) with the non-racemic triol (2) and pyridinium *p*-toluenesulfonate in hexanes gave a mixture of six cyclic acetals (33)–(38) in which no single isomer predominated. The minimum conformational energy of each acetal was computed (Macromodel), the results (Table 3) suggesting that the most stable are the two dioxolans (35) and (36), followed by the *trans* dioxan (34) (*trans* refers to the relationship between the alcohol-containing side chain and the phenyl group). This is consistent with the report[35] that the diastereoisomer of 2,4,6-trimethyl-2-phenyl-1,3-dioxan having the three methyl groups equatorial and the phenyl group axial is more stable than the epimer with an equatorial phenyl group.

Table 3. Computed minimized energies of (33)–(38)

Compound	Energy (kJ mol^{-1})
(33)	−10·27
(34)	−27·08
(35)	−37·28
(36)	−39·17
(37)	3·61
(38)	4·02

Comparison of selected peak heights in the ^{13}C n.m.r. spectrum indicated that mainly three isomers were present. The mixture of acetals was subjected to g.c.–m.s., the relative peak areas (Table 4) being consistent with the ^{13}C n.m.r. data. From the mass spectra the pairs of diastereoisomers could be identified, but the ring size of each pair could not be determined unequivocally.

Table 4. G.c.–m.s. data for (33)–(38) (thermodynamic mixture)

R_t (min)	Area (%)	Diastereoisomers
8·73	16·0	(33) or (34)
9·18	3·0	(37) or (38)
9·63	39	(35) or (36)
10·09	41	(35) or (36)
10·78	1	(37) or (38)

The only significant differences between the mass spectra were a fragment with *m/z* 131 for the single diastereoisomer (33) or (34), and fragments with *m/z* 121 for the pair of diastereoisomers (37)/(38). Since *m/z* 131 represents the loss of the phenyl group, this can occur from a compound with any of the ring sizes. Similarly, the fragment with *m/z* 121 ($PhCO^+$) is possible from any of the acetals. In order to simplify the structural assignment, the methoxy derivatives (39)–(44) were made (52%) from the mixture (33)–(38)

by treatment with sodium hydride and MeI. The resulting methyl ethers were subjected to g.c.–m.s., and their mass spectra were sufficiently different so that the ring sizes could now be determined (Table 5).

Table 5. Products from the methylation of (33)–(38) (thermodynamic mixture)

R_t (min)	Area (%)	Compound
7·75	19	(40)
7·85	33	(41) or (42)
8·05	38	(41) or (42)
9·48	4	(43) or (44)
9·56	4	(43) or (44)
9·79	1	(39)

Only the two dioxepans (43)/(44) gave mass spectra which contained a peak at *m/z* 72 but not at *m/z* 45 ($CH_2{=}O^+CH_3$). Only the dioxolans (41)/(42) and dioxans (39)/(40) can produce the latter fragment without rearrangement; similar initial fragmentation of (43)/(44) leads to *m/z* 72. The dioxans (39)/(40) were distinguished from the dioxolans (41)/(42) by the peak at *m/z* 177 (M − 45; stabilized more by resonance when produced from a dioxan rather than from a dioxolan).

In an attempt to minimize the number of acetals formed, acetalization of acetophenone was also attempted under kinetic control with trimethylsilyl trifluoromethanesulfonate as the catalyst.[16] In contrast to benzaldehyde, the reaction with the tris(silyl ether) (15) was very slow (−42 to −10°C, 31 h, 5% conversion). Reaction of (1,1-dimethoxyethyl)benzene (32) to give the acetal mixture (39)–(44) by the same method was much faster, (−42 to −23°C, 8 h, 46%). The three major isomers present in the thermodynamically controlled reaction were again formed, although in a different ratio (g.c.–m.s.) (Table 6).

Table 6. G.c.–m.s. data for (33)–(38) (kinetic mixture)

R_t (min)	Area (%)	Compound
9·14	34	(34) (*trans*-dioxan)
10·02	33	(35) or (36) (dioxolan)
10·46	14	(35) or (36) (dioxolan)

Table 7. ^{13}C n.m.r. peaks for the major acetals (34)–(36)

Position	*trans*-Dioxan (34)	Dioxolan (35) or (36)	Dioxolan (36) or (35)
C*ipso*	140·86	143·22	144·18
C*o* and C*m*	128·66	128·08	127·99
	126·64	125·04	124·91
C*p*	127·55	127·71	127·65
C4	70·72	74·44	75·35
C5 and CH_2OH	26·41	69·24	69·76
		59·97	60·03
C6 and CH_2OH	65·78		
	60·59		
C4–CH_2		35·91	35·53
C2–CH_3	32·67	28·17	28·05

The ^{13}C n.m.r. peaks for the three major isomers (Table 7) were assigned by comparison of the spectra of the mixtures formed under either kinetic or thermodynamic control. The signal sets for each dioxolan (35) and (36) are very similar, reflecting the diastereoisomeric nature of these acetals. The other major isomer was confirmed as dioxan (34) by comparison of its ^{13}C n.m.r. data with those of the *cis* dioxan (5) [C5; 26·41 ppm for (34), 26·7 ppm for (5)].

Frustratingly, separation of the mixture containing (34)–(36) on a preparative scale by flash chromatography could not be achieved. In an attempt to enable resolution, the (η^6-arene)tricarbonylchromium complexes were prepared [$Cr(CO)_6$, Bu_2O/tetrahydrofuran, 35%] from the acetal mixture resulting from thermodynamic control, but these derivatives were also inseparable (t.l.c.; hexanes/diethyl ether, 1:1, 14 elutions, one spot). A further attempt involved preparation of the t-butyldimethylsilyl ethers (Bu^tMe_2SiCl, $Pr^i{}_2NEt$, 20 h, room temp., 36%) of the complexed acetals, but again these derivatives could not be separated by column chromatography.

Improvement of the yields from the kinetically controlled acetalizations was then investigated by utilizing the tricarbonylchromium complexes (45) and (46) as substrates. During the preparation of the acyclic acetal complex (46) from (32) [$Cr(CO)_6$, Bu_2O/tetrahydrofuran] small amounts of the acetophenone complex (45) and of tricarbonyl[(1-methoxyethenyl)-η^6-benzene]chromium (47) were also formed. The acetalization of complex (45) proceeded faster than that of acetophenone itself, but the yield (−23°C, 5·5 h, 7%) was still too low. Similar treatment of the complex (46) gave (48)–(53) in only moderate yield (34%).

The envisaged application of this chemistry to the selective functionalization of an η^6-$Cr(CO)_3$ complex of acetophenone was frustrated because in none of the approaches investigated could a single acetal be made, with either kinetic or thermodynamic control affording an inseparable mixture of mainly the same three isomers. Although the benzaldehyde-derived acetal complex (16) could be obtained pure, deprotonation followed by quenching with either Me_3SiCl or MeI was neither regioselective nor high yielding. Consequently, (*S*)-butane-1,2,4-triol is not a useful non-racemic chiral auxiliary for the diastereoselective functionalization of (η^6-arene)tricarbonylchromium complexes of either benzaldehyde or acetophenone under the conditions reported.

Experimental

For general experimental details see ref. 1.

Dimethyl (S)*-2-Hydroxybutanedioate (3)*

(*S*)-Malic acid (1) (5·03 g, 37·5 mmol) was dissolved in dried methanol (60 ml), and concentrated hydrochloric acid (3 drops) added. The solution was left at room temperature for 5 days before silver(I) oxide (1 spatula) was added, and

the silver salts were filtered off. Workup and distillation (b.p. 90–100°C/>1 mmHg, lit.[36] 88–91°C/3 mmHg) gave dimethyl (*S*)-2-hydroxybutanedioate (3) as a colourless liquid (5·32 g, 88%). ν_{max} 3464 (OH), 2958, 1738 (C=O), 1440, 1222, 1173, 1109 cm^{-1}. δ_H 2·82–2·89 (d, *J* 4·2 Hz, (H 3)$_2$); 3·68 (br s, OH); 3·72 (s, OMe); 3·81 (s, OMe); 4·50–4·58 (dd, *J* 6·1, 4·7 Hz, H 2). δ_C 38·3 (C 3); 51·8 (OMe); 52·6 (OMe); 67·1 (C 2); 170·9 (C 1 or C 4); 173·6 (C 1 or C 4).

(S)-*Butane-1,2,4-triol (2)*

A solution of (*S*)-malic acid (1) (1·014 g, 7·57 mmol) in dry tetrahydrofuran (5·0 ml) was added slowly to a solution of $BH_3.SMe_2$ (2·2 ml, 23 mmol) and $B(OMe)_3$ (2·5 ml, 22 mmol) in dry tetrahydrofuran (5·0 ml), and then cooled in an ice–water bath. The mixture was left to stir at room temperature overnight. Methanol (6 ml) was added slowly and the solvents were removed; this process was repeated with more methanol (10 ml) to leave a colourless oil. Distillation (b.p. 152°C/0·4 mmHg, lit.[37] 120–130°C/0·1 mmHg) afforded (*S*)-butane-1,2,4-triol (2) (0·698 g, 87%). ν_{max} 3355 (OH), 2936, 1427, 1059 cm^{-1}. δ_H (CD_3OD) 1·51–1·80 (m, (H 3)$_2$); 3·42–3·52 (m, (H 4)$_2$); 3·65–3·83 (m, (H 1)$_2$, H 2).

(Dimethoxymethyl)benzene (4)

Benzaldehyde (2·9 ml, 29 mmol) and tungstosilicic acid (100 mg, 0·03 mmol) were dissolved in dry methanol (30 ml) and stirred at room temperature for 20 min. $NaBH_4$ (0·20 g, 5·3 mmol) was then added slowly. Workup and distillation (b.p. 40–45°C/<1 mmHg, lit.[38] 56–57°C/3·5 mmHg) gave (dimethoxymethyl)benzene (4) (2·73 g, 62%). ν_{max} 2937, 2830, 1454, 1355, 1206, 1105, 1055, 982, 912, 746 cm^{-1}. δ_H 3·30 (s, 2×OMe); 5·37 (s, Ph–C**H**); 7·28–7·39 (m, H*m*, H*p*); 7·39–7·48 (m, H*o*). δ_C 52·4 (OMe); 102·9 (Ph–**C**H); 126·5 (C*o* or C*m*); 128·0 (C*o* or C*m*); 128·2 (C*p*); 137·9 (C*ipso*).

*(2*S*,4*S*)-2-Phenyl-1,3-dioxan-4-methanol (5)*

(A) (Dimethoxymethyl)benzene (4) (0·85 ml, 5·7 mmol), (*S*)-butane-1,2,4-triol (2) (0·500 g, 5·6 mmol) and pyridinium *p*-toluenesulfonate (1 spatula) were refluxed in hexanes (20 ml) under a Dean–Stark separator for 7 h. Workup and flash chromatography (hexanes/Et_2O, 1 : 1) gave predominantly (2*S*,4*S*)-2-phenyl-1,3-dioxan-4-methanol (5) (0·97 g, 89%). *m/z* 194 (55%, M^+); 193 (59, M − H); 163 (77, M − CH_2OH); 107 (54); 105 (100, $PhCO^+$); 91 (56, $PhCH_2^+$); 79 (65); 77 (62, Ph^+); 71 (65, $C_4H_7O^+$). ν_{max} 3418 (OH), 2925, 2862, 1455, 1397, 1365, 1141, 1104, 1066, 1026, 758, 700 cm^{-1}. δ_H 1·32–1·39 (d, *J* 13·2 Hz, H 5*eq*); 1·76–1·88 (qd, *J* 12·4, 5·2 Hz, H 5*ax*); 2·70 (br s, OH); 3·54–3·60 (d, *J* 5·0 Hz, C**H**$_2$OH); 3·85–3·95 (m, H 4*ax*, H 6*ax*); 4·20–4·27 (ddd, *J* 11·4, 5·2, 0·9 Hz, H 6*eq*); 5·48 (s, H 2 of (5)); 5·75 (s, 0·045H, H 2 of *cis*-dioxolan (6)); 5·88 (s, 0·035H, H 2 of *trans*-dioxolan (7)); 7·30–7·38 (m, H*m*, H*p*); 7·45–7·49 (dd, *J* 7·5, 1·8 Hz, H*o*). δ_C 26·7 (C 5); 65·3 (CH_2OH); 66·4 (C 6); 77·4 (C 4); 101·1 (C 2); 126·0 (C*o*); 128·1 (C*m*); 128·8 (C*p*); 138·2 (C*ipso*). G.c.–m.s. (125°C for 20 min, 6°C per min to 250°C, 250°C for 15 min): 20·33 min [82%; *m/z* 194 (41%), 193 (50), 163 (70), 105 (100), 91 (42), 79 (64), 77 (67), 71 (43); due to (2*S*,4*S*)-2-phenyl-1,3-dioxan-4-methanol (5)]; 21·13 min [2%; *m/z* 194 (34%), 193 (52), 163 (57), 105 (100), 91 (48), 79 (66), 77 (75), 71 (52), 44 (88); due to (2*R*,4*S*)-2-phenyl-1,3-dioxan-4-methanol (8)]; 21·91 min [9%; *m/z* 194 (41%), 193 (76), 123 (26), 105 (100), 91 (61), 77 (59), 71 (98), 43 (89); due to (2*R*,4*S*)-2-phenyl-1,3-dioxolan-4-ethanol (6)]; 22·48 min [7%; *m/z* 194 (40%), 193 (59), 123 (34), 105 (100), 91 (58), 77 (58), 71 (97), 43 (9); due to (2*S*,4*S*)-2-phenyl-1,3-dioxolan-4-ethanol (7)].

(B) A solution (1·0 ml) of trimethlsilyl trifluoromethanesulfonate (0·05 ml, 0·26 mmol) in dry CH_2Cl_2 (10·0 ml) was cooled to −78°C. (*S*)-2,2,9,9-Tetramethyl-5-[(trimethylsilyl)oxy]-3,8-dioxa-2,9-disiladecane (15) (127 mg, 0·394 mmol) was added, followed by benzaldehyde (0·040 ml, 0·394 mmol). After stirring at this temperature for 3 h, the solution was warmed to −42°C for 4 h. Pyridine (3 drops) was added and the solution warmed to room temperature, poured into saturated aqueous $NaHCO_3$, and extracted three times with Et_2O. Workup gave predominantly (2*S*,4*S*)-2-phenyl-1,3-dioxan-4-methanol (5) (61 mg, 80%) as part of a mixture [(5)/(6)/(7) 98·3 : 1·1 : 0·6]. δ_H 5·53 (s, 0·983H, H 2 of (5)); 5·81 (s, 0·011H, H 2 of (6)); 5·94 (s, 0·006H, H 2 of (7)).

(C) A solution (1·0 ml) of trimethylsilyl trifluoromethanesulfonate (0·05 ml, 0·26 mmol) in dry CH_2Cl_2 (10·0 ml) was cooled to −42°C. The dioxadisiladecane (15) (160 mg, 0·497 mmol) was added, followed by (dimethoxymethyl)benzene (4) (0·075 ml, 0·50 mmol). The solution was stirred at this temperature for 4 h before pyridine (4 drops) was added. Workup and flash chromatography (hexanes/Et_2O, 1 : 1) gave predominantly (2*S*,4*S*)-2-phenyl-1,3-dioxan-4-methanol (5) (20 mg, 21%) as part of a mixture [(5)/(6)/(7) 80 : 12 : 8].

2,2,7,7-Tetramethyl-3,6-dioxa-2,7-disilaoctane (12)

A solution of ethane-1,2-diol (100 mg, 1·62 mmol) in CH_2Cl_2 (8·0 ml) was cooled in ice–water. Me_3SiCl (0·52 ml, 4·1 mmol) then Et_3N (0·68 ml, 4·9 mmol) were added dropwise. After the solution was stirred for 2 h at room temperature, Et_2O was added, the mixture filtered and the solvents were removed. This procedure was repeated three times to leave the dioxadisilaoctane (12) (0·208 g, 63%). ν_{max} 2958, 2868, 1252 (Si–C), 1148, 1099, 956, 841 (Si–C), 748 cm^{-1}. δ_H 0·30 (s, $SiMe_3$); 3·82 (s, (H 4)$_2$, (H 5)$_2$). δ_C −0·5 ($SiMe_3$); 63·9 (C 4, C 5).

2-Phenyl-1,3-dioxolan (11)

A solution (1·0 ml) of trimethylsilyl trifluoromethanesulfonate (0·03 ml, 0·16 mmol) in dry CH_2Cl_2 (10·0 ml) was cooled to −78°C. The dioxadisilaoctane (12) (148 mg, 0·718 mmol) and then benzaldehyde (0·075 ml, 0·74 mmol) were added. The solution was stirred for 4 h before pyridine (3 drops) was added. Workup afforded 2-phenyl-1,3-dioxolan (11) (58 mg, 54%). ν_{max} 2885, 1702 (PhCHO), 1458, 1400, 1220, 1069, 698 cm^{-1}. δ_H 3·98–4·19 (m, (H 4)$_2$, (H 5)$_2$); 5·81 (s, H 2); 7·32–7·41 (m, H*m*, H*p*); 7·44–7·51 (m, H*o*); 10·02 (s, 0·06H, PhCHO). δ_C 65·3 (C 4, C 5); 103·7 (C 2); 126·4 (C*o* or C*m*); 128·3 (C*o* or C*m*); 129·2 (C*p*); 129·7 (C*ipso*).

2,2,8,8-Tetramethyl-3,7-dioxa-2,8-disilanonane (14)

A solution of propane-1,3-diol (121 mg, 1·59 mmol) in CH_2Cl_2 (8·0 ml) was cooled in ice–water. Me_3SiCl (0·54 ml, 4·2 mmol) then Et_3N (0·70 ml, 5·0 mmol) were added dropwise. After 7 h, Et_2O was added, the slurry was filtered and the solvents were removed (three times) to leave the dioxadisilanonane (14) (0·328 g, 94%). ν_{max} 2957, 2870, 1251 (Si–C), 1092, 840 (Si–C), 747 cm^{-1}. δ_H 0·30 (s, $SiMe_3$); 1·86–2·00 (p, *J* 6·3 Hz, (H 5)$_2$); 3·81–3·89 (t, *J* 6·2 Hz, (H 4)$_2$, (H 6)$_2$). δ_C −0·6 ($SiMe_3$); 35·5 (C 5); 59·1 (C 4, C 6).

2-Phenyl-1,3-dioxan (13)

A solution (1·0 ml) of trimethylsilyl trifluoromethanesulfonate (0·05 ml, 0·26 mmol) in dry CH_2Cl_2 (10·0 ml) was cooled to −78°C. The dioxadisilanonane (14) (0·215 g, 0·977 mmol) and then benzaldehyde (0·10 ml, 0·99 mmol) were added. The solution was stirred at this temperature for 3·5 h then at −42°C for 3 h. Pyridine (5 drops) was added and the colourless solution warmed to room temperature. Workup gave 2-phenyl-1,3-dioxan (13) as a colourless liquid (84 mg, 53%). ν_{max} 2958, 2850, 1702 (PhCHO), 1454, 1377, 1146, 1103, 1006, 744, 696, 640 cm^{-1}. δ_H 1·36–1·48 (dtt, *J* 13·5, 2·6, 1·5 Hz, H 5*eq*); 2·18–2·34 (dtt, *J* 13·4, 12·3, 5·1 Hz, H 5*ax*); 3·88–4·05 (td, *J* 12·0, 2·5 Hz, H 4*ax*, H 6*ax*); 4·20–4·32 (ddt, *J* 10·5, 5·0, 1·3 Hz, H 4*eq*, H 6*eq*); 5·49 (s, H 2); 7·30–7·41 (m, H*m*, H*p*); 10·01 (s, 0·01H, PhC**H**O). δ_C 25·7 (C 5); 67·3

(C 4, C 6); 101·6 (C 2); 125·9 (C*o* or C*m*); 128·2 (C*o* or C*m*); 128·7 (C*p*); 138·7 (C*ipso*).

(S)-2,2,9,9-Tetramethyl-5-[(trimethylsilyl)oxy]-3,8-dioxa-2,9-disiladecane (15)

A solution of (*S*)-butane-1,2,4-triol (2) (0·522 g, 4·92 mmol) in CH_2Cl_2 (20 ml) was cooled in an ice bath. Me_3SiCl (2·20 ml, 17·3 mmol) and then Et_3N (3·10 ml, 22·3 mmol) were added dropwise to the stirred solution. Et_2O was added after 7 h, the reaction mixture filtered and the solvents were removed. More Et_2O was added, the slurry filtered and the solvent removed (twice more) to leave the dioxadisiladecane (15) (1·561 g, 99%). ν_{max} 2957, 2869, 1391, 1251 (Si–C), 1096, 1031, 842 (Si–C), 749, 685 cm^{-1}. δ_H 0·30 (s) and 0·31 (s, $SiMe_3$); 1·68–2·03 (m, (H 6)$_2$); 3·62–3·68 (dd, *J* 5·6, 1·6 Hz, (H 4)$_2$); 3·80–3·89 (dd, *J* 7·4, 5·9 Hz, (H 7)$_2$); 3·96–4·09 (dtd, *J* 8·2, 5·6, 4·0 Hz, H 5). δ_C 0·3 ($SiMe_3$); 37·0 (C 6); 59·0 (C 4 or C 7); 67·1 (C 4 or C 7); 70·2 (C 5).

Tricarbonyl[(dimethoxymethyl)-η^6-benzene]chromium (18)

(Dimethoxymethyl)benzene (4) (1·00 ml, 6·67 mmol) and $Cr(CO)_6$ (1·944 g, 8·84 mmol) were refluxed in Bu_2O (36·0 ml) and tetrahydrofuran (4·0 ml) under a flow of N_2 for 29 h. The cooled solution was filtered and the solvents were removed. Flash chromatography (hexanes/Et_2O, 4:1) gave the tricarbonyl chromium complex (18) (0·910 g, 47%) as a yellow oil which solidified on standing overnight, m.p. 37·5–39·5°C. ν_{max} 2939, 2835, 1965 and 1876 (CO), 1455, 1201, 1106, 1055, 663, 630, 535 cm^{-1}. δ_H 3·39 (s, OMe); 5·12 (s, Ph–C**H**); 5·24–5·40 (m, H*m*, H*p*); 5·47–5·56 (d, *J* 5·7 Hz, H*o*). δ_C 53·3 (OMe); 91·2 (C*o* or C*m*); 91·9 (C*o* or C*m*); 92·2 (C*p*); 101·3 (Ph–**C**H); 107·2 (C*ipso*); 232·4 ($Cr(CO)_3$).

Tricarbonyl[(2S,4S)-2-(η^6-phenyl)-1,3-dioxan-4-methanol]chromium (16)

(A) (2*S*,4*S*)-2-Phenyl-1,3-dioxan-4-methanol (5) (196 mg, 1·01 mmol) and $Cr(CO)_6$ (0·258 g, 1·17 mmol) were refluxed in Bu_2O (9·0 ml) and tetrahydrofuran (1·0 ml) under a flow of N_2 for 24 h. The cooled solution was filtered and the solvents were removed. Flash chromatography (hexanes/Et_2O, 1:2) three times (unresolved fractions were put back onto the column) gave tricarbonylchromium complex (16) (140 mg, 42%) as a thick yellow *oil* which solidified after standing for 1 month, m.p. 77·0–79·0°C (Found: $M^{+\bullet}$, 330·0198. $C_{14}H_{14}CrO_6$ requires $M^{+\bullet}$, 330·0196). *m/z* 330 (18%, M^+); 274 (24, M − 2CO); 246 (51, M − 3CO); 174 (56); 158 (37); 91 (27, $PhCH_2^+$); 52 (100, Cr^+). ν_{max} 3419 (OH), 2866, 1964 and 1876 (CO), 1361, 1104, 1024, 660 cm^{-1}. δ_H 1·42–1·47 (d, *J* 13·3 Hz, H 5*eq*); 1·83–1·96 (qd, *J* 12·5, 5·2 Hz, H 5*ax*); 2·25 (br s, OH); 3·63–3·76 (m, C**H**$_2$OH); 3·88–3·96 (td, *J* 12·0, 2·6 Hz, H 6*ax*); 3·96–4·04 (m, H 4*ax*); 4·24–4·29 (ddd, *J* 11·4, 5·1, 1·0 Hz, H 6*eq*); 5·22 (s, H 2); 5·25–5·44 (m, H*m*, H*p*); 5·45–5·68 (m, H*o*). δ_C 26·4 (C 5); 65·5 (CH_2OH); 66·6 (C 6); 77·7 (C 4); 91·3 (C*o* or C*m*); 91·4 (C*o* or C*m*); 92·7 (C*p*); 98·3 (C 2); 107·6 (C*ipso*); 232·7 ($Cr(CO)_3$).

(B) A solution (1·0 ml) of trimethylsilyl trifluoromethanesulfonate (0·05 ml, 0·26 mmol) in dry CH_2Cl_2 (10·0 ml) was cooled to −42°C. (The dioxadisiladecane (15) (143 mg, 0·444 mmol) was added followed by a solution of [(1,2,3,4,5,6-η)benzaldehyde]tricarbonylchromium (17) (109 mg, 0·450 mmol) in CH_2Cl_2 (1·0 ml). The solution was stirred for 3·5 h and then the temperature was raised to −23°C for 3 h. Et_3N (3 drops) was added and the mixture was warmed to room temperature. Workup and flash chromatography (hexanes/Et_2O, 1:2) gave the following. (i) Starting complex (17) (19 mg, 17%) was obtained as an orange oil. ν_{max} 1966 and 1886 (CO), 1694 cm^{-1} (C=O). (ii) The tricarbonylchromium complex (16) was obtained as a yellow oil (74 mg, 51%).

(C) A solution (1·0 ml) of trimethylsilyl trifluoromethanesulfonate (0·05 ml, 0·26 mmol) in dry CH_2Cl_2 (10 ml) was cooled to −42°C. The dioxadisiladecane (15) (154 mg, 0·478 mmol) was added followed by a solution of the tricarbonylchromium complex (18) (136 mg, 0·472 mmol) in dry CH_2Cl_2 (1·0 ml). The mixture was stirred for 7 h before Et_3N (3 drops) was added. Workup and flash chromatography (hexanes/Et_2O, 1:2) gave the tricarbonylchromium complex (16) (50 mg, 32%).

(2S,4S)-4-(Methoxymethyl)-2-phenyl-1,3-dioxan (19)

(A) The oil was removed from NaH (50% dispersion; 163 mg, 3·4 mmol) with hexanes, then tetrahydrofuran (10·0 ml) was added. A solution of dioxan (5) (0·330 g, 1·70 mmol) and imidazole (11 mg, 0·16 mmol) in tetrahydrofuran (5·0 ml) was added dropwise, and the reaction mixture refluxed for 1 h. After cooling the mixture to room temperature, MeI (0·28 ml, 4·5 mmol) was added and the reaction mixture stirred for 1 h before methanol (3 ml) was added. The solvents were removed and the residue was dissolved in CH_2Cl_2 and worked up. Flash chromatography (hexanes/Et_2O, 4:1) gave the (methoxymethyl)dioxan (19) as a yellow oil (166 mg, 47%). ν_{max} 2925, 2858, 1454, 1376, 1244, 1145, 1103, 1026, 996, 755, 699 cm^{-1}. δ_H 1·47–1·60 (d, *J* 13·3 Hz, H 5*eq*); 1·76–1·98 (qd, *J* 12·3, 5·1 Hz, H 5*ax*); 3·41 (s, OMe); 3·35–3·63 (m, C**H**$_2$OMe); 3·90–4·06 (td, *J* 11·8, 2·7 Hz, H 6*ax*); 4·03–4·16 (m, H 4*ax*); 4·23–4·34 (ddd, *J* 11·4, 5·1, 1·4 Hz, H 6*eq*); 5·53 (s, H 2); 7·30–7·38 (m, H*m*, H*p*); 7·46–7·53 (m, H*o*). δ_C 27·9 (C 5); 59·4 (OMe); 66·8 (C 6); 75·6 (C 4); 76·2 (**C**H_2OMe); 101·3 (C 2); 126·2 (C*o* or C*m*); 128·2 (C*o* or C*m*); 128·7 (C*p*); 138·2 (C*ipso*). G.c.–m.s. (130°C for 35 min, 10°C per min to 250°C, 250°C for 15 min): 22·88 min [1%; *m/z* 208 (14%, M^+), 207 (47, M − H), 105 (55, $PhCO^+$), 91 (25, $PhCH_2^+$), 45 (100, $CH_3O^+{=}CH_2$), 44 (69, $CH_2O^+{=}CH_2$); due to dioxolan]; 25·09 min [99%; *m/z* 208 (25%), 207 (18), 163 (100, $M^+ - C_2H_5O$), 105 (59), 91 (46), 77 (44, Ph^+), 45 (33)].

(B) Alcohol (5) (0·724 g, 3·73 mmol) was dissolved in dry dimethyl sulfoxide (6·0 ml). Powdered KOH (0·25 g, 4·46 mmol) was added to the stirred solution; after 30 min, MeI (1·3 ml, 21 mmol) was added and the solution was stirred for 19 h. The reaction mixture was then poured into water and extracted with Et_2O. Workup and flash chromatography (hexanes/Et_2O, 1:1) gave (i) (19) (44 mg, 6%); and (ii) starting material (100 mg, 14%).

(C) Alcohol (5) (105 mg, 0·541 mmol) was dissolved in dry tetrahydrofuran (2·0 ml) and cooled to −78°C. BuLi (1·80 mol l^{-1} in hexanes, 0·29 ml, 0·52 mmol) was added and the solution stirred for 10 min before MeI (0·06 ml, 0·96 mmol) was added. After 1 h the mixture was warmed to room temperature. Methanol (4 drops) was added and the solution diluted with CH_2Cl_2. Workup returned starting material (98 mg).

(D) Alcohol (5) (95 mg, 0·49 mmol) was dissolved in Et_2O (0·5 ml). Tetrabutylammonium iodide (2 mg, 0·005 mmol) was added followed by a solution of NaOH (79 mg, 2·0 mmol) in water (0·1 ml). The mixture was stirred for 20 min and the flask was then cooled in ice–water. Me_2SO_4 (0·10 ml, 1·1 mmol; filtered through K_2CO_3) was added carefully. After 6 h, concentrated aqueous ammonia (2 drops) was added; more water and Et_2O were added after a further 30 min. Workup and flash chromatography (hexanes/Et_2O, 4:1) gave (i) (19) (33 mg, 32%); and (ii) starting material (20 mg, 21%).

(E) The oil was removed from KH (24% dispersion; 0·81 g, 4·9 mmol) with hexanes, then tetrahydrofuran (3·0 ml) was added, followed by alcohol (5) (59 mg, 0·30 mmol). The mixture was stirred at room temperature for 2 h before MeI (0·20 ml, 3·2 mmol) was added. After the mixture was stirred overnight methanol (5 drops) was added, followed by CH_2Cl_2. Workup gave (19) (36 mg, 57%).

Methyl (2S,4S)-2-Phenyl-1,3-dioxan-4-ylmethyl Carbonate (20)

The alcohol (5) (54 mg, 0·28 mmol) was dissolved in dry dimethylformamide (3·0 ml). MeI (0·07 ml, 1·1 mmol) was added, followed by Ag_2O (unknown age; 0·204 g, 0·88 mmol). The mixture was stirred at room temperature for 45 h. Chloroform was added, and the solution was washed twice with 5% aqueous potassium cyanide, three times with water, then brine, and dried. Flash chromatography (hexanes/Et_2O, 4:1) gave the *carbonate* (20) (26 mg, 37%) (Found: $M^{+\bullet}$, 252·0991. $C_{13}H_{16}O_5$ requires $M^{+\bullet}$, 252·0998). *m/z* 252 (32%, M^+); 251 (25, M − H); 221 (10, M − OMe); 163 (26, M − $CH_2OCOOMe$); 105 (100, $PhCO^+$); 91 (31, $PhCH_2^+$); 77 (41, Ph^+); 71 (41). ν_{max} 2958, 28559, 1749 (C=O), 1444, 1273 (C–O), 1105, 995, 700 cm^{-1}. δ_H 1·49–1·61 (d, *J* 13·2 Hz, H5*eq*); 1·78–2·02 (qd, *J* 12·1, 5·1 Hz, H5*ax*); 3·79 (s, OMe); 3·91–4·06 (td, *J* 11·9, 2·6 Hz, H6*ax*); 4·10–4·37 (m, H4*ax*, H6*eq*, 4-CH_2O); 5·53 (s, H2); 7·32–7·39 (m, H*m*, H*p*); 7·45–7·53 (m, H*o*). δ_C 27·3 (C5); 54·9 (OMe); 66·4 (C6 or 4-CH_2O); 69·8 (C6 or 4-CH_2O); 74·5 (C4); 101·1 (C2); 126·1 (C*o* or C*m*); 128·2 (C*o* or C*m*); 128·8 (C*p*); 138·1 (C*ipso*).

(2S,4S)-4-(Methoxymethoxymethyl)-2-phenyl-1,3-dioxan (21)

(A) A solution of the alcohol (5) (80 mg, 0·41 mmol) in Pr^i_2NEt (1·0 ml, 5·8 mmol) was stirred at 0°C for 1·5 h. $BrCH_2OCH_3$ (0·05 ml, 0·61 mmol) was added dropwise, and the ice bath was removed after 1 h. After stirring at room temperature for 16 h, the mixture was poured onto ice–water and extracted into Et_2O. Workup and flash chromatography (hexanes/Et_2O, 1:1) gave the following compounds. (i) Benzaldehyde (13 mg, 30%). (ii) Starting material (18 mg, 23%). (iii) The ether (21) (15 mg, 15%). ν_{max} 2927, 1455, 1142, 1109, 1043, 755, 699 cm^{-1}. δ_H 1·47–1·65 (d, *J* 13·2 Hz, H5*eq*); 1·79–2·03 (qd, *J* 12·2, 5·2 Hz, H5*ax*); 3·38 (s, OMe); 3·53–3·80 (m, 4-CH_2O); 3·91–4·07 (td, *J* 11·9, 2·4 Hz, H6*ax*); 4·07–4·18 (m, H4*ax*); 4·23–4·39 (ddd, *J* 11·4, 5·2, 1·4 Hz, H6*eq*); 4·68 (s, O**C**H_2OMe); 5·54 (s, H2); 7·25–7·41 (m, H*m*, H*p*); 7·45–7·54 (m, H*o*).

(B) Oven-dried K_2CO_3 (82 mg, 0·59 mmol) was added to a solution of the alcohol (5) (98 mg, 0·51 mmol) and 18-crown-6 (3 mg, 0·01 mmol) in dry toluene (0·50 ml). $BrCH_2OCH_3$ (0·05 ml, 0·61 mmol) was added to the stirred solution, which was refluxed for 2 h. A large amount of benzaldehyde had formed (t.l.c.).

(C) Alcohol (5) (105 mg, 0·541 mmol) and *p*-TsOH (3 mg, 0·015 mmol) were dissolved in $CH_2(OMe)_2$ (2·0 ml, 23 mmol) and the solution was stirred overnight. A large amount of benzaldehyde had formed (t.l.c.).

(2S,4S)-4-[(t-Butyldimethylsilyl)oxy]methyl-2-phenyl-1,3-dioxan (22)

The alcohol (5) (98 mg, 0·51 mmol) was dissolved in dry CH_2Cl_2 (1·0 ml), and a solution of Bu^tMe_2SiCl (96 mg, 0·64 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (0·09 ml, 0·60 mmol) in dry CH_2Cl_2 (1·0 ml) was added. The mixture was stirred for 18 h before it was diluted with CH_2Cl_2 and washed quickly with small portions of ice-cold water, 0·25 mol l^{-1} HCl and saturated aqueous $NaHCO_3$. Solvent removal and flash chromatography (hexanes/Et_2O, 1:1) gave the following compounds. (i) Starting material (18 mg, 18%). (ii) The *silyl ether* (22) (70 mg, 45%) was also isolated (Found: $M^{+\bullet}$, 308·1792. $C_{17}H_{28}O_3Si$ requires $M^{+\bullet}$, 308·1808). *m/z* 251 (27%, M − Bu^t); 145 (100, $^+CH_2OSiMe_2Bu^t$); 117 (49); 105 (28, $PhCO^+$); 91 (94, $PhCH_2^+$); 75 (56); 59 (29). ν_{max} 2929, 2856, 1462, 1255 (Si–C), 1111, 1027, 837 (Si–C), 778, 697 cm^{-1}. δ_H 0·07 (s, $SiMe_2$); 0·91 (s, Bu^tSi); 1·57–1·69 (d, *J* 11·7 Hz, H5*eq*); 1·71–1·88 (qd, *J* 13·2, 5·0 Hz, H5*ax*); 3·76–3·81 (d, *J* 5·3 Hz, CH_2OSi); 3·86–4·04 (m, H4*ax*, H6*ax*); 4·25–4·36 (ddd, *J* 11·9, 4·9, 1·4 Hz, H6*eq*); 5·52 (s, H2); 7·31–7·38 (m, H*m*, H*p*); 7·45–7·53 (m, H*o*). δ_C 0·1 ($SiMe_2$); 18·3 (Si**C**Me_3); 25·9 (SiC**Me**$_3$); 28·3 (C5); 66·2 (C6 or CH_2OSi); 66·9 (C6 or CH_2OSi); 77·6 (C4); 101·1 (C2); 126·1 (C*o* or C*m*); 128·1 (C*o* or C*m*); 128·7 (C*p*); 138·6 (C*ipso*).

Tricarbonyl[(2S,4S)-4-(methoxymethyl)-2-(η^6-phenyl)-1,3-dioxan]chromium (23)

The dioxan (19) (144 mg, 0·692 mmol) and $Cr(CO)_6$ (0·220 g, 1·00 mmol) were refluxed in Bu_2O (9·0 ml) and tetrahydrofuran (1·0 ml) under a flow of N_2 for 16 h. The cooled solution was filtered and the solvents were removed. Flash chromatography (hexanes/Et_2O, 2:1) gave the following compounds. (i) Starting material (21 mg, 15%). (ii) The tricarbonylchromium complex (23) was obtained as a yellow *oil* (138 mg, 58%) (Found: $M^{+\bullet}$, 344·0349. $C_{15}H_{16}CrO_6$ requires $M^{+\bullet}$, 344·0352). *m/z* 344 (12%, M^+); 288 (24, M − 2CO); 260 (58, M − 3CO); 202 (33); 158 (84); 126 (41); 96 (29); 52 (100, Cr^+). ν_{max} 2929, 2869, 1964 and 1875 (CO), 1363, 1101, 1032, 737, 660, 629, 530 cm^{-1}. δ_H 1·45–1·61 (d, *J* 12·0 Hz, H5*eq*); 1·69–1·95 (m, H5*ax*); 3·35–3·65 (m including 3·41, s, OMe, C**H**$_2$OMe); 3·82–4·15 (m, H4*ax*, H6*ax*); 4·15–4·37 (m, H6*eq*); 5·12–5·45 (m, H2, H*m*, H*p*); 5·47–5·65 (m, H*o*). δ_C 27·5 (C5); 59·5 (OMe); 66·8 (C6); 75·1 (C4); 76·3 (**C**H_2OMe); 91·0 (Ph); 91·3 (Ph); 91·5 (Ph); 91·6 (Ph); 92·2 (Ph); 98·2 (C2); 106·5 (C*ipso*); 232·5 ($Cr(CO)_3$).

Tricarbonyl{(2S,4S)-4-[(t-butyldimethylsilyl)oxy]methyl-2-(η^6-phenyl)-1,3-dioxan}chromium (24)

The dioxan (22) (47 mg, 0·15 mmol) and $Cr(CO)_6$ (53 mg, 0·24 mmol) were refluxed in Bu_2O (9·0 ml) and tetrahydrofuran (1·0 ml) under a flow of N_2 for 23 h. The cooled mixture was filtered through Celite and the solvents were removed. Flash chromatography (hexanes/Et_2O, 1:1) gave the *tricarbonylchromium complex* (24) as a yellow oil (39 mg, 58%) (Found: $M^{+\bullet}$, 444·1071. $C_{20}H_{28}CrO_6Si$ requires $M^{+\bullet}$, 444·1060). *m/z* 444 (12%, M^+), 360 (100, M − 3CO), 317 (39), 275 (49), 169 (59), 126 (31), 52 (51, Cr^+). ν_{max} 2929, 2857, 1971 and 1888 (CO), 1472, 1362, 1254 (Si–C), 1110, 838 (Si–C), 778, 659, 629 cm^{-1}. δ_H 0·08 (s, $SiMe_2$); 0·90 (s, Bu^tSi); 1·52–1·94 (m, H5*eq*, H5*ax*); 3·54–4·00 (m, CH_2OSi, H4*ax*, H6*ax*); 4·19–4·33 (dd, *J* 11·1, 4·4 Hz, H6*eq*); 5·24 (s, H2); 5·26–5·38 (m, H*m*, H*p*); 5·47–5·59 (d, *J* 5·8 Hz, H*o*). δ_C 2·6 ($SiMe_2$); 18·3 (Si**C**Me_3); 25·9 (SiC**Me**$_3$); 27·8 (C5); 65·9 (CH_2OSi or C6); 66·9 (CH_2OSi or C6); 77·7 (C4); 90·8 (C*o* or C*m*); 91·8 (C*o* or C*m*); 91·9 (C*p*); 98·2 (C2); 108·0 (C*ipso*); 232·5 ($Cr(CO)_3$).

Deprotonation and D_2O Quench of Tricarbonyl[(2S,4S)-2-(η^6-phenyl)-1,3-dioxan-4-methanol]chromium (16)

(A) The tricarbonylchromium complex (16) (44 mg, 0·13 mmol) was dissolved in dry tetrahydrofuran (1·0 ml) in a flame-dried and nitrogen-flushed flask, and the solution was cooled to −78°C. Bu^tLi (1·45 mol l^{-1} in hexanes; 0·33 ml, 0·48 mmol) was added, followed 10 min later by D_2O (0·10 ml, 5·5 mmol). The solution was warmed to room temperature over 3 h. The solution was dried, filtered through Celite and the solvent removed to leave an oil which was dissolved in Et_2O and exposed to air and sunlight for 1 h. The mixture was filtered and the solvent removed to leave a pale yellow oil (27 mg, 100%). *m/z* 250 (2%), 198 (2), 197 (10), 196 (30), 195 (58), 194 (54), 193 (186), 167 (3), 166 (14), 165 (42), 164 (64), 163 (19), 110 (9), 109 (29), 108 (59), 107 (66), 106 (77), 105 (27), 92 (46), 80 (61), 71 (100), 57 (55). ν_{max} 3416 (OH), 2958, 2865, 1364, 1104, 1024, 634 cm^{-1}. δ_H 1·22–2·15 (m, H5*eq*, H5*ax*); 3·60–4·23 (m, C**H**$_2$OH, H4*ax*, H6*ax*); 4·23–4·39 (m, H6*eq*); 5·55 (s, 0·6H, H2); 7·27–7·58 (m, Ph–H).

(B) The complex (16) (42 mg, 0·13 mmol) was dissolved in tetrahydrofuran (1·0 ml) in a flame-dried and nitrogen-flushed

flask and cooled to −78°C. BuLi (1·18 mol l^{-1}; 0·38 ml, 0·45 mmol) was added, followed 20 min later by D_2O (0·05 ml, 2·8 mmol). The mixture was warmed to room temperature over 2 h, dried, filtered through Celite and the solvent removed to leave an orange oil (44 mg). This was dissolved in Et_2O and exposed to sunlight. Filtration and removal of the solvent afforded a colourless oil (21 mg, 85%). *m/z* 198 (1%), 197 (5), 196 (24), 195 (68), 194 (65), 193 (17), 167 (1), 166 (7), 165 (35), 164 (88), 163 (16), 110 (3), 109 (20), 108 (61), 107 (56), 106 (100), 105 (25), 92 (59), 80 (71), 78 (65), 71 (98), 57 (59). ν_{max} 3417 (OH), 2956, 2861, 1363·8, 1104, 1023, 633 cm^{-1}. δ_H 1·39–1·50 (d, *J* 13·2 Hz, H 5*eq*); 1·85–2·03 (qd, *J* 11·7, 5·4 Hz, H 5*ax*); 3·68 (br s, C**H**$_2$OH); 3·87–4·05 (m, H 4*ax*, H 6*ax*); 4·26–4·39 (ddd, *J* 11·4, 5·2, 1·2 Hz, H 6*eq*); 5·55 (s, 0·8H, H 2); 7·30–7·42 (m, H*m*, H*p*); 7·42–7·51 (m, 1·3H, H*o*).

(c) The complex (16) (28 mg, 0·085 mmol) was dissolved in dry Et_2O (1·5 ml) in a flame-dried and nitrogen-flushed flask, and cooled to −42°C; BuLi (2·09 mol l^{-1}; 0·15 ml, 0·31 mmol) was added. After 30 min D_2O (0·015 ml, 0·83 mmol) was added to the yellow solution/precipitate. After 1 h, the mixture was stirred at room temperature for 1 h before it was dried, filtered through Celite, and the solvent removed to leave a yellow-orange oil (27 mg). *m/z* 332 (3%), 331 (9), 330 (11), 275 (10), 274 (13), 247 (25), 246 (34), 175 (34), 174 (37), 159 (16), 158 (29), 157 (17), 112 (24), 52 (100, Cr^+). ν_{max} 3396 (OH), 2928, 1965 and 1866 (CO), 1361, 1105, 1026, 666, 631, 534 cm^{-1}. δ_H 1·20–1·69 (d, *J* 13·1 Hz, H 5*eq*); 1·75–2·08 (m, H 5*ax*); 2·23 (br s, OH); 3·58–4·09 (m, C**H**$_2$OH, H 4*ax*, H 6*ax*); 4·19–4·35 (m, H 6*eq*); 5·22 (s, 0·9H, H 2); 5·24–5·43 (m, H*m*, H*p*); 5·45–5·68 (m, 1·6H, H*o*).

*Deprotonation and Me_3SiCl Quench of Tricarbonyl[(2*S*,4*S*)-2-(η^6-phenyl)-1,3-dioxan-4-methanol]chromium (16)*

(a) The complex (16) (82 mg, 0·25 mmol) was dissolved in dry tetrahydrofuran (2·0 ml) in a flame-dried and nitrogen-flushed flask, and cooled to −78°C. BuLi (1·18 mol l^{-1}; 0·74 ml, 0·87 mmol) was added, and the yellow solution stirred for 1 h before Me_3SiCl (0·14 ml, 1·1 mmol) was added. The mixture was warmed slowly to room temperature over 1·5 h. Saturated aqueous $NaHCO_3$ (3 drops) was added to the brown solution, which was dried, filtered, and the solvent removed. Flash chromatography (hexanes/Et_2O, 4 : 1) gave the following fractions. (i) Tricarbonyl{(2*S*,4*S*)-2-(η^6-phenyl)-4-[(trimethylsilyl)oxy]methyl-1,3-dioxan}chromium (25) and (2*S*,4*S*)-2-phenyl-4-[(trimethylsilyl)oxy]methyl-1,3-dioxan (26) (15 mg, 15%). δ_H 0·13 (s, 9H, $OSiMe_3$); 1·20–1·85 (m, H 5*eq*, H 5*ax*); 3·55–4·07 (m, CH_2OSi, H 4*ax*, H 6*ax*); 4·18–4·36 (m, H 6*eq*); 5·20–5·38 (m, 2·8H, H 2, H*m*, H*p*); 5·48–5·61 (d, *J* 5·9 Hz, 1·5H, Ph–H); 7·28–7·55 (m, 1·7H, Ph–H). (ii) Tricarbonyl{(2*S*,4*S*)-2-[2-(trimethylsilyl)-η^6-phenyl]-1,3-dioxan-4-methanol}chromium (27) and (2*S*,4*S*)-2-[2-(trimethylsilyl)phenyl]-1,3-dioxan-4-methanol (28) (10 mg, 10%). δ_H 0·35 (s) and 0·38 (s, $SiMe_3$); 1·10–2·05 (m, H 5*ax*, H 5*eq*); 3·48–4·13 (m, C**H**$_2$OH, H 4*ax*, H 6*ax*); 4·13–4·41 (m, H 6*eq*); 5·15–5·75 (m, 2·6H, H 2, Cr–Ph–H); 7·28–7·53 (m, 2·4H, Ph–H). (iii) A *mixture* of tricarbonyl{(2*S*,4*S*)-4-[(trimethylsilyl)oxy]methyl-2-[2-(trimethylsilyl)-η^6-phenyl]-1,3-dioxan}chromium (29) and (2*S*,4*S*)-4-[(trimethylsilyl)oxy]-methyl-2-[2-(trimethylsilyl)phenyl]-1,3-dioxan (30) (47 mg) (Found: $M^{+\bullet}$, 474·0986. $C_{20}H_{30}CrO_6Si_2$ requires $M^{+\bullet}$, 474·0990. Found: $M^{+\bullet}$, 402·0586. $C_{17}H_{22}CrO_6Si$ requires $M^{+\bullet}$, 402·0591). *m/z* 474 (1), 402 (32), 318 (78), 214 (37), 163 (100), 126 (33), 73 (17, $^+SiMe_3$), 52 (83, Cr^+). ν_{max} 2955, 1966 and 1888 (CO), 1250 (Si–C), 1108, 841 (Si–C), 626 cm^{-1}. δ_H (C_6D_6) 0·15 (s), 0·20 (s), 0·22 (s, total 9H); 0·32 (s), 0·43 (s), 0·46 (s, total 9H); 0·98–1·06 (d, *J* 13·2 Hz, 0·7H); 1·16–1·29 (m, 0·9H); 1·57–1·93 (m, 1·8H); 3·58–3·72 (m, 2·3H); 3·77–3·88 (m, 1·2H); 3·95–4·02 (ddd, *J* 11·6, 5·2, 1·3 Hz, 0·4H); 4·04–4·12 (ddd, *J* 11·4, 5·1, 1·3 Hz, 0·8H); 4·39–4·43 (td, *J* 6·3, 1·1 Hz, 0·2H); 4·52–4·56 (t, *J* 6·4 Hz, 0·05H); 4·85–4·93 (td, *J* 6·5, 1·2 Hz, 0·3H); 5·05–5·13 (dd, *J* 6·4, 1·1 Hz, 0·3H); 5·41 (s, 0·2H); 5·49 (s, 0·1H); 5·55 (s), 5·56 (s, total 0·1H); 5·64–5·68 (dd, *J* 6·8, 1·0 Hz, 0·2H); 5·81 (s, 0·3H); 7·20–7·32 (m including C_6H_6, 1·9H); 7·32–7·47 (td, *J* 7·5, 1·4 Hz, 0·4H); 7·53–7·56 (dt, *J* 7·3, 1·3 Hz); 7·62–7·67 (dd, *J* 7·4, 0·9 Hz, 0·4H); 7·78–7·87 (m, 0·3H); 8·18–8·22 (dd, *J* 7·8, 1·3 Hz, 0·2H). δ_C (C_6D_6) −0·54; −0·35; 0·73; 0·83; 2·04; 27·56; 28·19; 65·44; 66·01; 66·17; 66·50; 66·63; 66·71; 66·77; 77·78; 77·90; 78·03; 89·20; 90·46; 94·55; 98·52; 99·78; 101·42; 126·74; 127·00; 129·34; 131·61; 134·45; 137·61; 144·96; 233·34; 233·60.

A solution of fraction (iii) in CH_2Cl_2 was exposed to sunlight for 4 h. Filtration through Celite and removal of the solvent gave the alcohol (28) and the disilyl compound (30) (14 mg). ν_{max} 3453 (OH), 2956, 1364, 1250 (Si–C), 1105, 839 (Si–C), 757 cm^{-1}. δ_H ($CDCl_3$) 0·11 (s, 2·3H, $OSiMe_3$); 0·35 (s, $CSiMe_3$); 1·41–1·53 (d, *J* 13·2 Hz, H 5*eq*); 1·86–2·08 (m, H 5*ax*); 3·63–4·06 (m, CH_2OH, H 4*ax*, H 6*ax*); 4·25–4·35 (ddd, *J* 11·3, 5·1, 1·4 Hz, 1H, H 6*eq*); 5·72, (s, H 2); 7·28–7·55 (m, 3H, Ph–H); 7·68–7·75 (d, *J* 7·6 Hz, Ph–H). δ_C ($CDCl_3$) 0·6 ($SiMe_3$); 26·7 (C 5); 65·7 (CH_2OH and CH_2OSi, or C 6); 66·5 (CH_2OH and CH_2OSi, or C 6); 77·6 (C 4); 101·0 (C 2); 126·2 (Ph); 128·3 (Ph); 129·4 (Ph); 134·2 (Ph).

(b) The complex (16) (110 mg, 0·333 mmol) was dissolved in dry Et_2O (2·0 ml) in a flame-dried and nitrogen-flushed flask, and cooled to −78°C. BuLi (1·18 mol l^{-1}; 1·00 ml, 1·18 mmol) was added slowly. After 1 h Me_3SiCl (0·20 ml, 1·57 mmol) was added, and the mixture was stirred for 1 h before warming to room temperature. Saturated aqueous $NaHCO_3$ (10 drops) was added. Workup and flash chromatography (hexanes/Et_2O, 4 : 1) gave compounds (27)–(30) as a yellow oil (32 mg). ν_{max} 1966 and 1888 (CO), 1251 (Si–C), 1109, 841 cm^{-1} (Si–C). δ_H 0·10 (s, 17H); 0·38 (s, 13H); 1·13–1·28 (t, *J* 7·0 Hz, 1·6H); 1·50–1·95 (m, 3·5H); 3·40–4·08 (m, 7·6H); 4·21–4·39 (m, 1·1H); 5·08–5·19 (m, 0·5H); 5·33 (s, 0·7H); 5·37–5·48 (m, 0·8H); 5·50–5·70 (m, 2·0H); 7·30–7·50 (m, 2·0H). δ_C −0·57; 0·64; 27·69; 28·11; 65·17; 65·64; 66·59; 66·79; 77·57; 77·98; 88·98; 90·39; 94·78; 98·19; 99·96; 100·95; 101·19; 126·10; 128·16; 128·72; 129·29; 134·17; 233·05 ($Cr(CO)_3$).

A solution of the yellow oil in CH_2Cl_2 was exposed to the sunlight for 3 h until the yellow colour had disappeared. Filtration through Celite and removal of the solvent gave a *mixture* of (28) and (30) as a colourless oil (15 mg) (Found: $MH^{+\bullet}$, 339·1823. $C_{17}H_{31}O_3Si_2$ requires $MH^{+\bullet}$, 339·1812. Found: $MH^{+\bullet}$, 267·1427. $C_{14}H_{23}O_3Si$ requires $MH^{+\bullet}$, 267·1416). *m/z* 339 (16%), 267 (100), 235 (18), 163 (84). ν_{max} 3486, 2957, 1372, 1250 (Si–C), 1107, 839 (Si–C), 757 cm^{-1}. δ_H 0·11 (s), 0·12 (s), 0·14 (s, total 11H); 0·34 (s, 4·4H); 0·35 (s, 5·6H); 0·82–0·98 (m, 0·6H); 1·39–1·54 (d, *J* 13·2 Hz, 0·9H); 1·55–2·09 (m, 4·0H); 3·52–3·83 (m, 3·1H); 3·87–4·06 (m, 2·6H); 4·22–4·36 (m, 1·1H); 5·52 (s, 0·1H); 5·55 (s, 0·1H); 5·67 (s, 0·4H); 5·72 (s, 0·3H); 7·28–7·43 (m, 3·1H); 7·44–7·55 (m, 1·8H); 7·68–7·76 (d, *J* 7·7 Hz, 0·7H). G.c. (180°C for 20 min, 10°C per min up to 250°C, 250°C for 15 min): 4·67 min {21%; due to dioxan (30)}; 11·76 min {79%; due to dioxan (28)}.

*Deprotonation and MeI Quench of Tricarbonyl[(2*S*,4*S*)-2-(η^6-phenyl)-1,3-dioxan-4-methanol]chromium (16)*

(a) The complex (16) (76 mg, 0·23 mmol) was dissolved in dry Et_2O (2·0 ml) in a flame-dried and nitrogen-flushed flask, and cooled to −78°C. BuLi (1·18 mol l^{-1}, 0·69 ml, 0·81 mmol) was added, and the solution stirred for 1 h. MeI (0·065 ml, 1·04 mmol) was then added and the reaction mixture slowly warmed to room temperature over 2 h. Saturated aqueous $NaHCO_3$ (3 drops) was added, and the solution dried, filtered through Celite, and the solvent removed to leave starting

material (16) (87%) and decomplexed starting material (5) (13%) as a yellow oil (77 mg).

(B) The complex (16) (56 mg, 0·17 mmol) was dissolved in dry Et_2O (1·0 ml) in a flame-dried and nitrogen-flushed flask, and cooled to −78°C. BuLi (1·18 mol l^{-1}; 0·51 ml, 0·60 mmol) was added. The temperature was raised to 0°C after 15 min. After a further 1·5 h, the yellow precipitate was cooled again to −78°C. MeI (0·12 ml, 1·91 mmol) was added and the reaction mixture warmed slowly to room temperature over 2 h. Saturated aqueous $NaHCO_3$ (3 drops) was added. Workup gave starting material (16) (26%) and decomplexed starting material (5) (74%) as a yellow oil (46 mg).

(C) The complex (16) (55 mg, 0·17 mmol) was dissolved in dry Et_2O (1·0 ml) in a flame-dried and nitrogen-flushed flask, and cooled to −78°C. BuLi (1·18 mol l^{-1}; 0·49 ml, 0·58 mmol) was added, producing a yellow precipitate which was stirred for 30 min before $CuBr.SMe_2$ (121 mg, 0·59 mmol) was added. After a further 30 min, MeI (0·10 ml, 1·6 mmol) was added. The precipitate became brown and the mixture was warmed to room temperature over 4 h. Saturated aqueous $NaHCO_3$ (3 drops) was added. Workup gave the starting material (16) (83%) and decomplexed starting material (5) (17%) as a yellow oil (75 mg).

(D) The complex (16) (100 mg, 0·30 mmol) was dissolved in dry Et_2O (2·0 ml) in a flame-dried and nitrogen-flushed flask, and cooled to −78°C. Bu^tLi (1·45 mol l^{-1}; 0·73 ml, 1·1 mmol) was added. After 5 min, MeI (0·20 ml, 3·2 mmol) was added and the reaction mixture was warmed to room temperature over 3 h. Saturated aqueous $NaHCO_3$ (3 drops) was added. Workup gave the starting material (16) (73%) and decomplexed starting material (5) (27%) as a dark brown oil (88 mg).

Deprotonation and MeOTf Quench of Tricarbonyl[(2S,4S)-2-(η^6-phenyl)-1,3-dioxan-4-methanol]chromium (16)

(A) The complex (16) (99 mg, 0·30 mmol) was dissolved in dry Et_2O (2·0 ml) in a flame-dried and nitrogen-flushed flask, and cooled to −78°C. BuLi (1·18 mol l^{-1}; 0·89 ml, 1·05 mmol) was added, and the solution stirred for 1 h. MeOTf (0·16 ml, 1·4 mmol) was added and the reaction mixture was warmed to room temperature over 4 h before saturated aqueous $NaHCO_3$ (3 drops) was added. The solution was dried, filtered through Celite and the solvent removed. Flash chromatography (hexanes/CH_2Cl_2, 1:2) gave the following compounds. (i) The tricarbonylchromium complex (17) (19 mg, 26%) was obtained as an orange oil. ν_{max} 2964, 1980 and 1908 (CO), 1698 (C=O), 1337 cm^{-1}. δ_H 5·21–5·32 (t, *J* 6·2 Hz, H*m*); 5·63–5·70 (t, *J* 6·2 Hz, H*p*); 5·89–5·95 (d, *J* 6·4 Hz, H*o*); 9·46 (s, PhCHO). (ii) The tricarbonyl chromium complex (23) was obtained as a yellow oil (50 mg, 48%). (iii) Starting material (16) (12 mg, 12%).

(B) The complex (16) (60 mg, 0·17 mmol) was dissolved in dry Et_2O (1·5 ml) in a flame-dried and nitrogen-flushed flask, and cooled to −78°C. BuLi (1·18 mol l^{-1}; 0·37 ml, 0·44 mmol) was added, producing a yellow precipitate. The temperature was raised to 0°C after 5 min and the precipitate became brown. After 1 h the mixture was cooled again to −78°C, then MeOTf (0·10 ml, 0·85 mmol) was added. After the mixture was warmed to room temperature over 3 h, saturated aqueous $NaHCO_3$ (3 drops) was added. Workup and flash chromatography (hexanes/CH_2Cl_2, 2:1) gave the (methoxymethyl)dioxan (19) and (2*S*,4*S*)-4-(methoxymethyl)-2-(2-methylphenyl)-1,3-dioxan [decomplexed (31)] as a pale yellow oil (13 mg). δ_H 1·48–1·60 (d, *J* 13·3 Hz, H 5*eq*); 1·77–1·98 (qd, *J* 12·3, 5·1 Hz, H 5*ax*); 2·39 (s, 0·7H, Ph–Me); 3·33–3·64 (m including 3·41, s, OMe, CH_2OMe); 3·90–4·15 (m, H 4*ax*, H 6*ax*); 4·24–4·36 (ddd, *J* 11·4, 5·1, 1·3 Hz, H 6*eq*); 5·53 (s, H 2); 7·11–7·23 (m, Ph–H); 7·31–7·37 (m, Ph–H); 7·46–7·53 (m, 1·5H, Ph–H).

(C) The complex (16) (104 mg, 0·32 mmol) was dissolved in dry Et_2O (2·0 ml) in a flame-dried and nitrogen-flushed flask, and cooled to −78°C. BuLi (1·18 mol l^{-1}; 0·94 ml, 1·1 mmol) was added, and after 10 min, the temperature was raised to −23°C for 1 h. MeOTf (0·16 ml, 1·4 mmol) was added, and the mixture was slowly warmed to room temperature over 2 h. Saturated aqueous $NaHCO_3$ (3 drops) was added. Workup and flash chromatography (hexanes/CH_2Cl_2, 1:2) gave the following compounds. (i) The benzaldehyde (17) (38 mg, 49%). (ii) Starting material (16) (4 mg, 4%). (iii) A mixture of compound (17) and tricarbonyl{(2*S*,4*S*)-4-(methoxymethyl)-2-(2-methyl-η^6-phenyl)-1,3-dioxan}chromium (31) was obtained as an oil (39 mg). δ_H 1·48–1·60 (d, *J* 13·3 Hz, H 5*eq*); 1·77–1·98 (qd, *J* 12·3, 5·1 Hz, H 5*ax*); 2·24 (s, 0·1H, Cr–Ph**Me**); 2·39 (s, 0·3H, Ph**Me**); 3·33–3·64 (m including 3·41, s, OMe, C**H**$_2$OMe); 3·91–4·15 (m, H 4*ax*, H 6*ax*); 4·24–4·37 (ddd, J 11·4, 5·2, 1·3 Hz, H 6*eq*); 5·22–5·33 (m, Cr–Ph–H); 5·52–5·63 (m, Cr–Ph–H); 7·12–7·22 (m, 0·3H, Ph–H); 7·29–7·40 (m, 1·7H, Ph–H); 7·46–7·52 (m, 0·1H, Ph–H).

Deprotonation and Me_3SiCl Quench of Tricarbonyl[(2S,4S)-4-(methoxymethyl)-2-(η^6-phenyl)-1,3-dioxan]chromium (23)

The tricarbonylchromium complex (23) (103 mg, 0·299 mmol) was dissolved in dry Et_2O (2·0 ml) in a flame-dried and nitrogen-flushed flask, and cooled to −78°C. BuLi (1·18 mol l^{-1}; 0·64 ml, 0·755 mmol) was added and the solution stirred for 1 h. Me_3SiCl (0·14 ml, 1·1 mmol) was added, the reaction mixture was warmed to room temperature over 2 h, and saturated aqueous $NaHCO_3$ (8 drops) was added. Workup and flash chromatography (hexanes/Et_2O, 2:1) gave (i) decomplexed starting material (19) (16 mg, 26%); and (ii) starting material (23) (13 mg, 13%).

Deprotonation and D_2O Quench of Tricarbonyl{(2S,4S)-4-[(t-butyldimethylsilyl)oxy]methyl-2-(η^6-phenyl)-1,3-dioxan}-chromium (24)

The tricarbonylchromium complex (24) (12 mg, 0·027 mmol) was dissolved in dry Et_2O (1·0 ml) in a flame-dried and nitrogen-flushed flask, and cooled to −42°C. BuLi (2·09 mol l^{-1}, 0·038 ml, 0·079 mmol) was added and the yellow solution stirred for 30 min before D_2O (0·015 ml, 0·83 mmol) was added. After 1·5 h, the reaction mixture was warmed to room temperature for 1 h. Workup gave a yellow oil (11 mg). *m/z* 446 (5%), 445 (12), 444 (8), 361 (100), 360 (71), 318 (40), 317 (26), 276 (50), 275 (37), 169 (88), 127 (38), 126 (45), 52 (82, Cr^+). ν_{max} 2929, 1971 and 1893 (CO), 1255 (Si–C), 1110, 838 (Si–C), 628 cm^{-1}. δ_H 0·08 (s, $SiMe_2$); 0·90 (s, Bu^tSi); 1·51–2·00 (m, H 5*eq*, H 5*ax*); 3·55–4·05 (m, CH_2OSi, H 4*ax*, H 6*ax*); 4·21–4·39 (m, H 6*eq*); 5·24 (s, H 2); 5·26–5·37 (m, H*m*, H*p*); 5·51–5·57 (m, 1·5H, H*o*).

(1,1-Dimethoxyethyl)benzene (32)

Acetophenone (1·325 g, 11·0 mmol), trimethyl orthoformate (1·50 ml, 13·7 mmol) and *p*-TsOH (17 mg, 0·090 mmol) were dissolved in methanol (30 ml) in a flask equipped with a Vigreaux column. The solution was stirred and heated with a Bunsen burner, and a colourless liquid distilled across at 60–65°C. K_2CO_3 was added, and the solution was diluted with CH_2Cl_2. Workup gave (1,1-dimethoxyethyl)benzene (32) as a yellow liquid (1·825 g, 100%). ν_{max} 2991, 2942, 2830, 1448, 1276, 1147, 1092, 1042, 877, 765, 701 cm^{-1}. δ_H 1·54 (s, C–CH_3); 3·19 (s, OMe); 7·26–7·39 (m, H*m*, H*p*); 7·46–7·53 (m, H*o*). δ_C 26·0 (Me); 48·9 (OMe); 101·6 (Ph–C); 126·2 (H*o* or H*m*); 127·5 (H*p*); 128·0 (H*o* or H*m*); 142·8 (H*ipso*).

(2S,4S)-2-Methyl-2-phenyl-1,3-dioxan-4-methanol (33) and Isomers (34)–(38)

(A) (1,1-Dimethoxyethyl)benzene (32) (5·43 g, 32·7 mmol), (*S*)-butane-1,2,4-triol (2) (3·00 ml, 33·7 mmol) and pyridinium

p-toluenesulfonate (1 spatula) were mixed in hexanes (50 ml) and refluxed under a Dean–Stark separator for 5 h, until 1·2 ml of methanol had collected. The cooled solution was diluted with CH_2Cl_2. Workup and flash chromatography (hexanes/Et_2O, 1:1) gave a *mixture* of the dioxan (33) and isomers (34)–(38) (3·315 g, 49%). (Found: $MH^{+\bullet}$, 209·1176. $C_{12}H_{17}O_3$ requires $MH^{+\bullet}$, 209·1178). *m/z* 209 (26%, MH^+), 193 (100, M − Me), 131 (21), 121 (42), 105 (63, $^+$PhCO), 77 (18, Ph), 71 (53, $C_4H_7O^+$). ν_{max} 3420 (OH), 2935, 1447, 1372, 1247, 1179, 1069, 1026, 765, 702 cm^{-1}. δ_H 1·18–1·24 (dtd, *J* 13·0, 2·4, 1·6 Hz, 0·2H); 1·50 (s), 1·52 (s), 1·53 (s, total 0·9H); 1·58–1·96 (m including 1·63 (s) and 1·66 (s), 5·0H); 2·28 (br s, 0·1H); 2·60 (br s, 0·4H); 2·70 (br s, 0·6H); 3·39–3·51 (t, *J* 8·3 Hz, 0·5H); 3·55–4·00 (m including 3·65–3·70 (dd, *J* 7·8, 6·4 Hz), 3·71–3·77 (t, *J* 5·8 Hz), 3·77–3·81 (t, *J* 5·4 Hz) and 3·86–3·90 (dd, *J* 7·8, 6·9 Hz), 4·0H); 4·06–4·13 (m, 0·4H); 4·15–4·21 (dd, *J* 8·2, 6·0 Hz, 0·5H); 4·33–4·42 (tdd, *J* 8·2, 5·8, 5·0 Hz, 0·4H); 7·23–7·51 (m, 5·0H). Major product, 41%, one diastereoisomer of (4*S*)-2-methyl-2-phenyl-1,3-dioxolan-4-ethanol (35) or (36) δ_C 28·05 (2-Me); 35·53 (4–CH_2); 60·03 (C 5 or CH_2OH); 69·76 (C 5 or CH_2OH); 75·35 (C 4); 109·09 (C 2); 124·91 (C*o* or C*m*); 127·65 (C*p*); 127·99 (C*o* or C*m*); 144·18 (C*ipso*). Second major product, 39%, other diastereoisomer of the dioxolan (35) or (36) δ_C 28·17 (2-Me); 35·91 (4-CH_2); 59·97 (C 5 or CH_2OH); 69·24 (C 5 or CH_2OH); 74·44 (C 4); 109·05 (C 2); 125·04 (C*o* or C*m*); 127·71 (C*p*); 128·08 (C*o* or C*m*); 143·22 (C*ipso*). Third major product, 16·0%, one diastereoisomer of (4*S*)-2-methyl-2-phenyl-1,3-dioxan-4-methanol (33) or (34) δ_C 26·41 (C 5); 32·60 (2-Me); 60·59 (C 6 or CH_2OH); 65·78 (C 6 or CH_2OH); 70·72 (C 4); 100·87 (C 2); 126·64 (C*o* or C*m*); 127·55 (C*p*); 128·66 (C*o* or C*m*); 140·86 (C*ipso*). Minor isomers δ_C 26·97 (Me); 27·20 (Me); 37·37 (CH_2); 37·72 (CH_2); 57·52 (CH_2); 58·68 (CH_2); 59·31 (CH_2); 65·27 (CH_2); 66·43 (CH_2); 67·77 (CH); 67·90 (CH); 69·69 (CH_2); 124·61 (CH); 125·53 (CH); 125·64 (CH); 127·50 (CH); 127·58 (CH); 127·89 (CH); 127·95 (CH). G.c.–m.s. (150°C for 10 min, 5°C per min up to 250°C, 250°C for 15 min): 8·73 min [16%; *m/z* 193 (66%), 131 (41), 105 (82), 77 (34), 71 (88), 43 (100); due to one diastereoisomer of the dioxan (33) or (34)]; 9·18 min [3%; *m/z* 193 (65%), 121 (86), 105 (93), 77 (37), 71 (29), 43 (100); due to one diastereoisomer of (5*S*)-2-methyl-2-phenyl-1,3-dioxepan-5-ol (37) or (38)]; 9·63 min [39%; *m/z* 193 (76%), 105 (81), 77 (32), 71 (100), 43 (82); due to one diastereoisomer of (4*S*)-2-methyl-2-phenyl-1,3-dioxolan-4-ethanol (35) or (36)]; 10·09 min [41%; *m/z* 193 (85%), 105 (99), 77 (35), 71 (100), 43 (73); due to other diastereoisomer of the dioxolan (35) or (36)]; 10·78 min [1%; *m/z* 193 (70%), 121 (14), 105 (100), 77 (35), 71 (59), 43 (73); due to other diastereoisomer of the dioxepan (37) or (38)].

(B) A solution (1·0 ml) of trimethylsilyl trifluoromethanesulfonate (0·01 ml, 0·052 mmol) in dry CH_2Cl_2 (10 ml) was cooled to −78°C. The dioxadisiladecane (15) (182 mg, 0·565 mmol) was added followed by acetophenone (0·07 ml, 0·60 mmol). After 7 h, pyridine (3 drops) was added and the solution warmed to room temperature. Workup gave acetophenone (179 mg).

Repetition of this reaction at −42°C, or −42 to −20 to −10°C, gave acetophenone and a small amount of a mixture of the dioxans/dioxolans/dioxepans (33)–(38).

(C) A solution (1·0 ml) of trimethylsilyl trifluoromethanesulfonate (0·05 ml, 0·26 mmol) in dry CH_2Cl_2 (10·0 ml) was cooled to −42°C. The dioxadisiladecane (15) (156 mg, 0·484 mmol) was added followed by (1,1-dimethoxyethyl)benzene (32) (87 mg, 0·524 mmol). After 5 h, the temperature was raised to −23°C for 3 h. Pyridine (3 drops) was added and the reaction mixture warmed to room temperature. Workup and flash chromatography (hexanes/Et_2O, 1:1) gave the dioxan (33) and isomers (34)–(38) as a pale yellow oil (46 mg, 46%). ν_{max} 3453 (OH), 2954, 1447, 1372, 1251, 1184, 1070, 1029, 764, 703 cm^{-1}. δ_H 1·19–1·25 (d, *J* 12·9 Hz, 0·7H); 1·46–1·99 (m including 1·54 (s), 1·64 (s) and 1·67 (s), 7·4H); 2·30 (br s, 0·6H); 3·13–4·45 (m including 3·67–3·72 (dd, *J* 7·8, 6·3 Hz) and 4·18–4·22 (dd, *J* 8·3, 5·9 Hz), 6·3H); 7·26–7·51 (m, 5·0H). Major product, 34%, one diastereoisomer of the dioxan (33) or (34) δ_C 26·41 (C 5); 32·70 (2-Me); 60·65 (C 6 or CH_2OH); 65·98 (C 6 or CH_2OH); 70·67 (C 4); 100·96 (C 2); 126·74 (C*o* or C*m*); 127·64 (C*p*); 128·75 (C*o* or C*m*); 140·97 (C*ipso*). Second major product, 33%, one diastereoisomer of the dioxolan (35) or (36) δ_C 28·27 (2-Me); 35·90 (4-CH_2); 60·38 (C 5 or CH_2OH); 69·34 (C 5 or CH_2OH); 74·80 (C 4); 109·19 (C 2); 125·14 (C*o* or C*m*); 127·82 (C*p*); 128·18 (C*o* or C*m*); 143·28 (C*ipso*). Third major product, 14%, other diastereoisomer of the dioxolan (35) or (36) δ_C 28·16 (2-Me); 35·50 (4-CH_2); 60·50 (C 5 or CH_2OH); 69·86 (C 5 or CH_2OH); 75·72 (C 4); 109·23 (C 2); 125·00 (C*o* or C*m*); 127·75 (C*p*); 128·10 (C*o* or C*m*); 144·25 (C*ipso*). Other isomers δ_C 27·52 (Me); 28·34 (Me); 36·34 (CH_2); 36·76 (CH_2); 59·20 (CH_2); 59·38 (CH_2); 61·00 (CH_2); 69·54 (CH_2); 70·01 (CH); 70·87 (CH); 73·47 (CH); 125·20 (CH); 127·49 (CH); 127·99 (CH); 128·28 (CH); 128·54 (CH); 128·63 (CH); 128·95 (CH). G.c.–m.s. (150°C for 13 min, 5°C per min up to 250°C, 250°C for 15 min): 9·14 min [34%; *m/z* 193 (65%), 131 (38), 105 (80), 77 (34), 71 (86), 43 (100); due to one diastereoisomer of the dioxan (33) or (34)]; 10·02 min [33%; *m/z* 193 (82%), 105 (85), 77 (36), 71 (100), 43 (84); due to one diastereoisomer of the dioxolan (35) or (36)]; 10·46 min [14%; *m/z* 193 (87%), 105 (95), 77 (40), 71 (100), 43 (76); due to other diastereoisomer of the dioxolan (35) or (36)].

(2S,4S)-4-(Methoxymethyl)-2-methyl-2-phenyl-1,3-dioxan (39) and Isomers (40)–(44)

The oil was removed from NaH (50% dispersion; 55 mg, 1·1 mmol) with hexanes, then dry tetrahydrofuran (10·0 ml) was added. A solution of the acetal mixture (33)–(38) (from thermodynamic control; 111 mg, 0·534 mmol) and imidazole (1 spatula) in dry tetrahydrofuran (5·0 ml) was added. The mixture was refluxed for 1 h, cooled to room temperature, and MeI (0·10 ml, 1·6 mmol) was added. After the mixture was stirred overnight, methanol (1 ml) was added. Workup and flash chromatography (hexanes/Et_2O, 1:1) gave compounds (39)–(44) (61 mg, 52%). ν_{max} 3060, 2987, 2875, 1448, 1371, 1185, 1118, 1027, 882, 765, 702 cm^{-1}. δ_H 1·18–1·37 (m, 1·0H); 1·48–2·05 (m including 1·54 (s), 1·62 (s), 1·65 (s) and 1·72 (s), 6·2H); 3·28–4·40 (m including 3·29 (s), 3·32 (s), 3·41 (s), 3·61–3·69 (dd, *J* 7·6, 6·5 Hz), 3·82–3·90 (dd, *J* 7·5, 6·6 Hz), 3·98–4·06 (t, *J* 6·3 Hz) and 4·12–4·20 (dd, *J* 8·2, 6·0 Hz), 7·6H); 7·24–7·50 (m, 5·0H). δ_C 27·44; 28·29; 28·30; 32·76; 33·54; 33·92; 58·67; 59·36; 60·90; 69·37; 69·46; 69·96; 73·61; 74·77; 76·00; 125·08; 125·18; 125·80; 126·80; 127·52; 127·62; 127·99; 128·09; 128·69. G.c.–m.s. (130°C for 20 min, 5°C per min up to 250°C, 250°C for 15 min): 7·75 min [19·0%; *m/z* 207 (77%), 177 (51), 145 (45), 105 (93), 85 (100), 71 (75), 45 (44), 43 (90); due to one diastereoisomer of (4*S*)-4-(methoxymethyl)-2-methyl-2-phenyl-1,3-dioxan (39) or (40)]; 7·85 min [33%; *m/z* 207 (89%), 145 (28), 105 (84), 77 (24), 45 (100), 43 (43); due to one diastereoisomer of (4*S*)-4-(methoxyethyl)-2-methyl-2-phenyl-1,3-dioxolan (41) or (42)]; 8·05 min [38%; *m/z* 207 (94), 145 (12), 105 (100), 77 (25), 45 (96), 43 (34); due to other diastereoisomer of (4*S*)-4-(2-methoxyethyl)-2-methyl-2-phenyl-1,3-dioxolan (41) or (42)]; 9·48 min [4%; *m/z* 207 (9%), 121 (21), 105 (24), 72 (100), 43 (23); due to one diastereoisomer of (5*S*)-5-methoxy-2-methyl-2-phenyl-1,3-dioxepan (43) or (44)]; 9·56 min [4%; *m/z* 207 (8%), 121 (21), 105 (25), 72 (100), 43 (25); due to other diastereoisomer of the dioxepan (43) or (44)]; 9·79 min [1%; *m/z* 207 (65%), 177 (37), 105 (100), 85 (70), 71 (47), 45 (25), 43 (59); due to other diastereoisomer of the dioxan (39) or (40)].

Attempted Synthesis of (2S,4S)-4-(Methoxymethoxymethyl)-2-methyl-2-phenyl-1,3-dioxan and Isomers

The oil was removed from NaH (50% dispersion; 58 mg, 1·2 mmol) with hexanes, and dry tetrahydrofuran (10·0 ml) was added. A solution of the acetal mixture (33)–(38) (from thermodynamic control; 118 mg, 0·567 mmol) and imidazole (1 spatula) in dry tetrahydrofuran (5·0 ml) was added slowly. The mixture was refluxed for 1 h and $BrCH_2OCH_3$ (0·14 ml, 1·7 mmol) was added. After the mixture was stirred overnight, methanol (1 ml) was added. Workup and flash chromatography (hexanes/Et_2O, 9 : 1) gave (i) acetophenone (35 mg, 51%); and (ii) starting material (48 mg, 41%).

Tricarbonyl[(2S,4S)-2-methyl-2-(η^6-phenyl)-1,3-dioxan-4-methanol]chromium (48) and Isomers (49)–(53)

(A) The acetal mixture (33)–(38) (from thermodynamic control; 0·521 g, 2·50 mmol) and $Cr(CO)_6$ (0·801 g, 3·64 mmol) were refluxed in Bu_2O (18·0 ml) and tetrahydrofuran (2·0 ml) under a flow of nitrogen until a green tinge appeared. Workup and flash chromatography (hexanes/Et_2O, 3 : 7) gave a *mixture* of the isomers (48)–(53) as a yellow oil (0·304 g, 35%) (Found: $M^{+\bullet}$, 344·0348. $C_{15}H_{16}CrO_6$ requires $M^{+\bullet}$, 344·0352). *m/z* 344 (17%, M^+), 260 (53, M − 3CO), 188 (47), 172 (37), 126 (29), 105 (25, $PhCO^+$), 52 (100, Cr^+). ν_{max} 3389 (OH), 2948, 2887, 1963 and 1866 (CO), 1413, 1177, 1052, 660, 631, 538 cm^{-1}. δ_H 1·50–2·03 (m including 1·60, (s) and 1·63 (s), 5·0H); 3·62–3·93 (m including 3·64–3·72 (t, *J* 7·9 Hz), 1·8H); 4·14–4·31 (ddd, *J* 16·4, 7·9, 5·7 Hz, 1·2H); 4·32–4·55 (m, 0·1H); 5·09–5·19 (t, *J* 6·2 Hz, 2H, H*m*); 5·41–5·52 (m, 1H, H*p*); 5·67–5·74 (d, *J* 6·1 Hz, 2H, H*o*). δ_C 27·8; 29·7; 34·5; 35·4; 60·0; 70·2; 75·5; 75·8; 88·8; 93·0; 95·0; 95·4; 107·0; 232·7 ($Cr(CO)_3$).

(B) A solution (1·0 ml) of trimethylsilyl trifluoromethanesulfonate (0·05 ml, 0·26 mmol) in dry CH_2Cl_2 (10 ml) was cooled to −23°C. The dioxadisiladecane (15) (141 mg, 0·438 mmol) was added followed by a solution of tricarbonyl[1-(η^6-phenyl)ethanone]chromium (45) (105 mg, 0·410 mmol) in CH_2Cl_2 (1·0 ml). The solution was stirred for 5·5 h before Et_3N (3 drops) was added and the mixture warmed to room temperature. Workup and flash chromatography (hexanes/Et_2O, 1 : 1) gave (i) the tricarbonylchromium complex (45) (74 mg, 70%) as an orange oil; and (ii) the isomers (48)–(53) (10 mg) as a yellow oil.

(C) A solution (1·0 ml) of trimethylsilyl trifluoromethanesulfonate (0·05 ml, 0·26 mmol) in dry CH_2Cl_2 (10·0 ml) was cooled to −23°C. The dioxadisiladecane (15) (159 mg, 0·494 mmol) then a solution of tricarbonyl[(1,1-dimethoxyethyl)-η^6-benzene]-chromium (46) (141 mg, 0·467 mmol) in CH_2Cl_2 (1·0 ml) were added. The solution was stirred for 8 h before Et_3N (4 drops) was added and the reaction mixture warmed to room temperature. Workup and flash chromatography (hexanes/Et_2O, 1 : 1) gave the following compounds. (i) The tricarbonylchromium complex (45) (19 mg, 16%). (ii) The isomers (48)–(53) as a yellow oil (54 mg, 34%). ν_{max} 3392 (OH), 2950, 2887, 1963 and 1875 (CO), 1413, 1176, 1052, 660 631, 536 cm^{-1}. δ_H 1·58–1·74 (m including 1·61 (s) and 1·64 (s), 4·7H); 1·74–2·12 (m including 1·84–1·94 (q, *J* 5·9 Hz), 4·4H); 3·63–3·75 (t, *J* 7·7 Hz, 1·3H); 3·84 (br s, 2·7H); 4·15–4·32 (ddd, *J* 16·0, 7·9, 5·8 Hz, 1·2H); 4·32–4·58 (m, 0·7H); 5·11–5·21 (t, *J* 6·3 Hz, 2·1H, H*m*); 5·43–5·53 (m, 0·9H, H*p*); 5·67–5·78 (dd, *J* 6·8, 0·8 Hz, 2·0H, H*o*). δ_C 28·0; 29·9; 34·5; 35·4; 60·2; 70·3; 70·4; 75·6; 76·0; 88·4; 88·6; 92·9; 93·2; 95·0; 95·4; 232·7 ($Cr(CO)_3$).

Tricarbonyl{(2S,4S)-4-[(t-butyldimethylsilyl)oxy]methyl-2-methyl-2-(η^6-phenyl)-1,3-dioxan}chromium and Isomers

Pr^i_2NEt (0·04 ml, 0·23 mmol) was added to a solution of the complexed acetal mixture (48)–(53) (54 mg, 0·16 mmol) and Bu^tMe_2SiCl (30 mg, 0·20 mmol) in CH_2Cl_2 (1·5 ml), and the mixture was stirred for 20 h at room temperature. Workup and flash chromatography (hexanes/Et_2O, 1 : 1) gave the tricarbonylchromium complex and its isomers as a yellow oil (26 mg, 36%). ν_{max} 2954, 2857·4, 1970 and 1889 (CO), 1256 (Si–C), 1094, 837 (Si–C), 658 cm^{-1}. δ_H 0·05 (s, 6H, $SiMe_2$); 0·89 (s, 9H, Bu^tSi); 1·59 (s) and 1·62 (s, total 3H, 2-Me); 1·75–1·96 (m, 2H); 3·58–3·83 (m, 4H); 4·11–4·40 (m, 2H); 5·09–5·23 (t, *J* 6·1 Hz, 2H, H*m*); 5·38–5·50 (t, *J* 6·0 Hz, 1H, H*p*); 5·74–5·78 (d, *J* 6·3 Hz, 2H, H*o*). δ_C −2·3 ($SiMe_2$); 18·2 (Si**C**Me_3); 25·9 ($SiMe_2$); 28·2 (Me); 28·3 (Me); 29·7 (Me); 35·0 (CH_2); 36·4 (CH_2); 36·9 (CH_2); 59·8 (CH_2); 69·8 (CH_2); 70·5 (CH_2); 70·7 (CH_2); 73·7 (CH); 75·0 (CH); 75·3 (CH); 88·3 (CH); 88·4 (CH); 88·6 (CH); 88·8 (CH); 92·8 (CH); 92·9 (CH); 93·1 (CH); 94·9 (CH); 99·3 (C); 100·5 (C); 106·5 (C); 113·6 (C); 113·8 (C); 119·9 (C); 232·7 ($Cr(CO)_3$).

Tricarbonyl[(1,1-dimethoxyethyl)-η^6-benzene]chromium (46)

(1,1-Dimethoxyethyl)benzene (32) (0·996 g, 6·00 mmol) and $Cr(CO)_6$ (1·986 g, 9·03 mmol) were refluxed in Bu_2O (36·0 ml) and tetrahydrofuran (4·0 ml) under a flow of N_2 for 39 h. Workup and flash chromatography (hexanes/Et_2O, 9 : 1) gave the following compounds. (i) Tricarbonyl[(1-methoxyethenyl)-η^6-benzene]chromium (47) was obtained as a yellow solid (114 mg, 7%), m.p. 63–65°C. ν_{max} 2938, 1963 and 1879 (CO), 1616 (C=C), 1313, 1258, 1124, 1038, 658, 629 cm^{-1}. δ_H 3·71 (s, OMe); 4·26 (s, one of $=CH_2$); 4·59 (s, one of $=CH_2$); 5·12–5·55 (m, Ph–H); 5·55–5·90 (m, Ph–H). δ_C 55·6 (OMe); 83·1 ($=CH_2$); 89·8 (C*o* or C*m*); 91·8 (C*o* or C*m*); 94·2 (C*p*); 98·9 (C*ipso*); 163·9 (C=); 232·7 ($Cr(CO)_3$). (ii) The tricarbonylchromium complex (46) was obtained as a yellow crystalline *solid* (0·96 g, 53%), m.p. 96–98°C (Found: $M^{+\bullet}$, 302·0250. $C_{13}H_{14}CrO_5$ requires $M^{+\bullet}$, 302·0246). *m/z* 302 (12%, M^+), 271 (22, M − OMe), 218 (27, M − 3CO), 186 (49), 135 (44), 114 (55), 52 (100, Cr^+). ν_{max} 3093, 2968, 1976 and 1887 (CO), 1456, 1038, 635, 537 cm^{-1}. δ_H 1·61 (Me); 3·20 (2×OMe); 5·13–5·23 (t, *J* 6·5 Hz, H*m*); 5·41–5·48 (t, *J* 6·3 Hz, 1H, H*p*); 5·75–5·80 (d, *J* 6·0 Hz, H*o*). δ_C 25·9 (Me); 49·0 (OMe); 89·1 (C*o* or C*m*); 93·9 (C*o* or C*m*); 94·6 (C*p*); 99·5 (Ph–**C**); 111·7 (C*ipso*); 232·7 ($Cr(CO)_3$). (iii) The tricarbonylchromium complex (45) (15 mg, 1%). ν_{max} 1970 and 1900 (CO), 1687 cm^{-1} (C=O). δ_H 2·46 (COMe); 5·23–5·31 (t, *J* 6·5 Hz, H*m*); 5·60–5·68 (t, *J* 6·3 Hz, H*p*); 6·03–6·08 (d, *J* 6·0 Hz, H*o*).

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