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Rhodium-Carbenoid Mediated O-H Insertion Reactions. O-H Insertion *vs.* H-Abstraction and Effect of Catalyst

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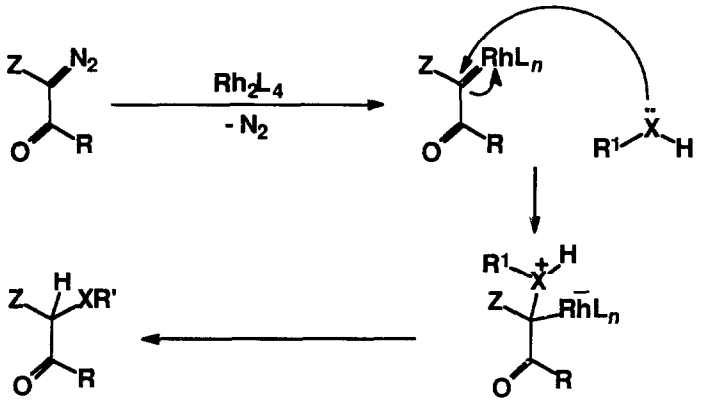
Abstract: The synthesis and rhodium mediated O-H insertion reactions of a wide range of diazo compounds are described. The rate at which the diazo compounds decompose in the presence of 2-propanol and the rhodium catalyst is strongly dependent on the electron withdrawing group(s) attached to the diazo carbon, with diazophosphonates being the least reactive. Insertion into the O-H bond of methanol, t-butanol and phenols was also investigated, as well as the effect of catalyst. In some cases 'reduction' of the diazo group to the corresponding CH_2 group competes with O-H insertion, although this is highly catalyst and substrate dependent. Of the catalysts used, rhodium(II) trifluoroacetamide is the most effective for O-H insertion reactions.

The transition metal catalysed decomposition of diazo compounds, first discovered over 80 years ago, has now become a standard procedure in organic synthesis.[1] Indeed synthetic uses of diazo compounds, particularly diazo carbonyl compounds,[2] in organic synthesis have increased dramatically in recent years as a result of the development of new transition-metal catalysts which have supplanted the original copper-based catalysts such as copper powder, copper bronze, copper(II) sulfate and copper(II) bis-(1,3-diketonates). Rhodium(II) carboxylates, first introduced by Teyssié and co-workers in the early 1970s,[3] are amongst the most efficient catalysts for the decomposition of α-diazo carbonyl compounds, and are now widely used in synthetic transformations such as cyclopropanation and C-H insertion. The recent development of chiral rhodium based catalysts has further increased the use of such reactions in organic synthesis.[4]

Our own interest in the rhodium carbenoid mediated process centres on the so-called X-H insertion reaction (X = NR, O, S), particularly in its intramolecular mode,[5] although recently we have also studied intermolecular O-H insertion reactions.[6] Such reactions involving O-H insertion have also been investigated by others under photochemical,[7] and copper[8] or rhodium[9] catalysed conditions. Although the rhodium catalysed reaction is a formal insertion of the metallocarbenoid into the X-H bond, it is perhaps better considered as involving nucleophilic attack by the heteroatom lone pair on the highly electrophilic carbenoid followed by hydrogen shift (Scheme 1). However, the precise details of the process are not known, and for example, prior or simultaneous coordination of the nucleophile to the metal may also be involved.[10]

In our successful use of such rhodium carbenoid mediated reactions in the cyclisation of diazo alcohols as a route to functionalised medium ring ethers,[5] we found that the nature of the Z-group markedly affected the rate of the cyclisation reaction as monitored by thin layer chromatography (TLC). We have now carried out a more detailed study of the rhodium(II) carboxylate catalysed decomposition of various diazo compounds in the presence of hydroxylic compounds to determine how the nature of the groups attached to the diazo carbon affect the intermolecular O-H insertion reaction.



Scheme 1

RESULTS AND DISCUSSION

Preparation of Diazo Compounds

In order to probe the substituent effects, a range of diazo compounds containing different electron withdrawing groups was required; diazo compounds **1** - **13** were chosen. With the exception of ethyl diazoacetate **1** (which is commercially available) and ethyl 2-diazo-3-phenylpropanoate **3**, all of the diazo compounds used within this study were prepared from the analogous methylene compounds by diazo-transfer techniques (see Table 1). Ethyl diazophenylacetate **2** was prepared by activation of the corresponding methylene group in the precursor by formylation and then treatment with base and tosyl azide (Method A).[11] The diazo compound **3** was prepared by the silver(I) oxide promoted alkylation of ethyl diazoacetate with benzyl bromide (Method B).[12,13] Ethyl *N,N*-dimethylcarbamoyl diazoacetate **4** was prepared by acylation of dimethylamine with the diazo acid chloride **14** (Method C).[14] Ethyl diazocyanoacetate **5**, was prepared using a mixture of the reagent **15** and sodium azide as the diazo-transfer agent (Method D).[12] Diethyl diazomalonate **6**,[12] ethyl phenylsulfonyldiazoacetate **7**[12,15] and ethyl diazoacetoacetate **12**[12] were each prepared using 4-methylbenzenesulfonyl azide (tosyl azide, **16**) and triethylamine (Method E). Ethyl diphenylphosphinyl-diazoacetate **8** was also prepared using tosyl azide but potassium *tert*-butoxide was used as the base (Method F).[12,16] In the preparation of the triethyl diazophosphonoacetate **9**,[12,17] diethyl phenylsulfonyl(diazomethyl)phosphonate **10**,[17] bis-(benzenesulfonyl)diazomethane **13**[18] and bis-(diethyl phosphono) diazomethane **11**,[12,17] the use of sodium hydride as base was necessary (Method G). Alternatively, the diazo compounds **8** and **9** were also prepared from the corresponding methylene compounds using the commercially available diazo-transfer reagent azidotris-(diethylamino)phosphonium bromide and a catalytic amount of potassium t-butoxide.[19]

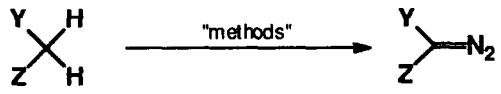
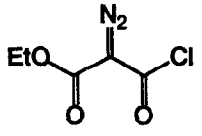


Table 1. Preparation of Diazo Compounds

Compound	Y	Z	Method[a]	Yield (%)	Reference
1	H	CO_2Et	Available	-	-
2	Ph	CO_2Et	A	92	11
3	$PhCH_2$	CO_2Et	B	35	12,13
4	Me_2NCO	CO_2Et	C	70	14
5	C≡N	CO_2Et	D	80	12
6	CO_2Et	CO_2Et	E	95	12
7	$PhSO_2$	CO_2Et	E	70	12,15
8	Ph_2PO	CO_2Et	F	50	12,16
9	$(EtO)_2PO$	CO_2Et	G	63	12,17
10	$PhSO_2$	$(EtO)_2PO$	G	88	17
11	$(EtO)_2PO$	$(EtO)_2PO$	G	78	12,17
12	COMe	CO_2Et	E	80	12
13	$PhSO_2$	$PhSO_2$	G	62	18

[a] For method, see text.



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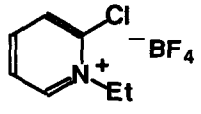

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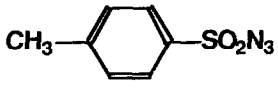

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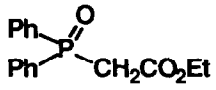

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Insertion Reactions into 2-Propanol

Each of the diazo compounds **1-11** underwent reaction with 2-propanol when treated with specific rhodium catalysts (Table 2). Generally, the diazo substrate was treated with the appropriate catalyst (1 mol%) and 2-propanol (120 equiv) in dichloromethane solvent. If no reaction occurred, then the mixture was heated under reflux. The progress of these reactions was carefully monitored by TLC and the time taken for the disappearance of all of the diazo substrate was noted. Under these conditions each of the diazo compounds **1-9** was readily decomposed using 1 mol% of the commercially available rhodium(II) acetate, leading to the insertion product (Table 2). In the case of the diazo substrate **8** the yield of the insertion product was low due to the competing hydrogen abstraction leading to the "reduced" product **17**, the methylene precursor to the diazo

compound. However when the reaction was repeated in the presence of rhodium(II) trifluoroacetamide as catalyst (see below, also), then a mixture of the O-H insertion product **25** (45%) and **17** (15%) was obtained. This troublesome side reaction involving "reduction"of the diazo compound also occurred to a lesser extent in other procedures.

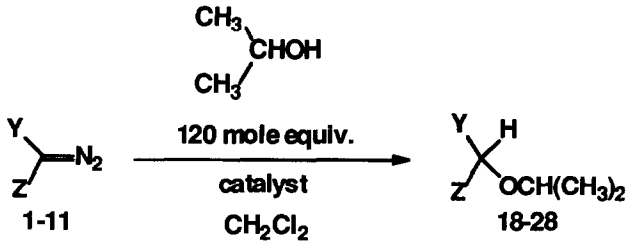


Table 2. Rhodium Mediated Insertion Reactions of Diazo Compounds into 2-Propanol

Diazo	Y	Z	Product	Temp (°C)	Catalyst	Yield (%)	Time (h)
1	H	CO_2Et	**18**	RT	$Rh_2(OAc)_4$	64	0.5
2	Ph	CO_2Et	**19**	RT	$Rh_2(OAc)_4$	92	0.1
3	$PhCH_2$	CO_2Et	**20**	RT	$Rh_2(OAc)_4$	32	2.0
4	Me_2NCO	CO_2Et	**21**	RT	$Rh_2(OAc)_4$	66	32
5	C≡N	CO_2Et	**22**	RT	$Rh_2(OAc)_4$	86	3.0
6	CO_2Et	CO_2Et	**23**	RT	$Rh_2(OAc)_4$	66	125.0
7	$PhSO_2$	CO_2Et	**24**	RT	$Rh_2(OAc)_4$	64	18.0
8	Ph_2PO	CO_2Et	**17**	reflux	$Rh_2(OAc)_4$	30	1.0
8	Ph_2PO	CO_2Et	**25**	RT	$Rh_2(tfacm)_4$	45	22.5
9	$(EtO)_2PO$	CO_2Et	**26b**	reflux	$Rh_2(OAc)_4$	83	10.0
10	$PhSO_2$	$(EtO)_2PO$	**27**	110[a]	$Rh_2(OAc)_4$	67	72
10	$PhSO_2$	$(EtO)_2PO$	**27**	110[a]	$Rh_2(tfacm)_4$	79	2.0
11	$(EtO)_2PO$	$(EtO)_2PO$	**28**	110[a]	$Rh_2(tfacm)_4$	81	2.0

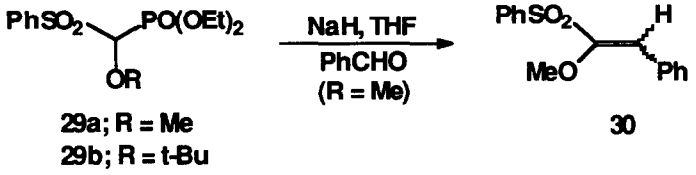
Notes. [a]These reactions were carried out in dry toluene at reflux.

The diazo compound **9**, which is stabilised on one side by a phosphonate group and on the other by an ester moiety, failed to undergo any appreciable decomposition at room temperature in the presence of rhodium(II) acetate but underwent a smooth insertion reaction when heated in the refluxing mixture. The diazophosphonate **11** proved to be stable towards decomposition with such a catalyst, even at the elevated temperature. However, as we have previously shown, rhodium(II) trifluoroacetamide $[Rh_2(tfacm)_4]$[20] is a far superior catalyst for such processes.[6b] This was again demonstrated here when this catalyst decomposed the diazophosphonates **10** and **11** leading to the insertion products **27** and **28** in good yield. Ethyl diazoacetoacetate **12** decomposed rapidly (2 h) under the reaction conditions to afford a mixture of products which could not be separated; likewise the bis-sulfonyl diazo compound **13** produced a black intractable tar.

The products of insertion of the intermediate rhodium carbenoids into the O-H bond of 2-propanol are the isopropyloxy compounds **18** to **28**. These were easily identified by their ^1H NMR spectra, in which the methine proton of the isopropyl group occurred as a heptet between δ 3.50 and 4.00 and the other proton α to

oxygen appeared as a singlet *ca.* δ 4.0-5.0 (or a doublet, with characteristic splitting, if the CH- was also adjacent to phosphorus).

The diazo phosphonate sulfone **10** was also decomposed photochemically in the presence of alcohols. Irradiation in 2-propanol resulted exclusively in H-abstraction (90%). However, irradiation of **10** in methanol or t-butanol gave the corresponding alkoxy phosphonates **29a** and **29b** in 63 and 44% yield respectively. The structure of the methoxy phosphonate **29a** was further proved by a Wadsworth-Emmons olefination reaction with benzaldehyde to give the sulfonyl vinyl ether **30** as a mixture of E/Z-isomers (*ca.* 95:5; 56%)(Scheme 2).



29a; R = Me
29b; R = t-Bu

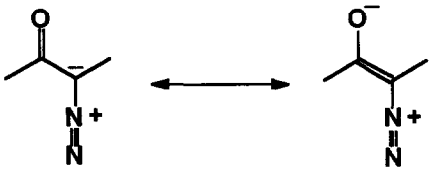
30

Scheme 2

The results indicate that the stability of the diazo compounds towards rhodium catalysts in 2-propanol is critically dependent on the diazo substituent, and decreases in the order:

$$PO(OEt)_2 > Ph_2PO > EtO_2C \sim PhSO_2 > Me_2NCO > CN > PhCH_2 > Ph \sim H$$

Some years ago Regitz compared the *thermal* stabilities of several substituted diazomethanes and noted the increased stability of of diazo phosphonates over diazo carbonyl compounds.[21] This was explained by considering the two mesomers **A** and **B** of α-diazo carbonyl compounds (Figure 1).



A **B**

Figure 1

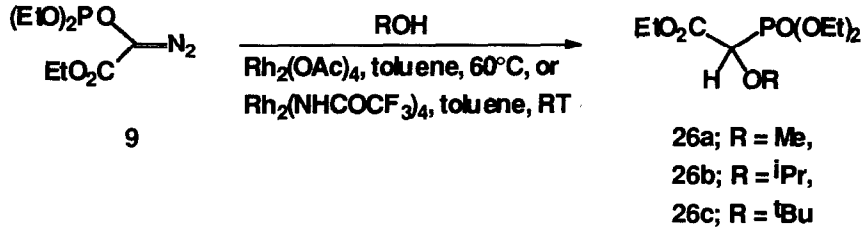
Diazo carbonyls are able to mesomerise easily between keto and enolate forms; in the latter delocalisation of the negative charge away from the diazo group leaves it isolated. Diazophosphonates, because of the nature of the P=O bond, do not mesomerise in a similar manner, and therefore there is a much greater interaction of positive and negative charges around the diazo group resulting in less isolated diazo character and increased stability. Applying this model to rhodium(II) acetate catalysed decompositions, greater stabilisation of charges in the diazophosphonate means that the diazo carbon is less nucleophilic for the initial interaction with the vacant coordination site on rhodium, the first step in the formation of the metallocarbenoid.

Insertion Reactions into the O-H Bond of other Compounds

We were also interested in determining the relative reactivity of different types of O-H group in, for example, primary, secondary and tertiary alcohols and phenols. In his initial communication in 1973, Teyssié

reported that ethyl diazoacetate **1** showed some selectivity when added to equimolar mixtures of different alcohols in the presence of rhodium(II) acetate.[3] Ethanol (relative reactivity = 2.12) appeared to be approximately twice as reactive as t-butanol (relative reactivity = 1.00) towards the rhodium carbenoid, whilst 2-propanol (relative reactivity = 1.20) and t-butanol showed approximately equal reactivity towards the same species. This reactivity order is the order of increasing acidity as well as the order of decreasing steric hindrance. If the coordination affinities of these alcohols for the catalyst were similar then one might have predicted such an order of reactivity. In order to confirm such results we carried out a similar series of competition reactions using diazophosphonate **9**.

Treatment of the diazophosphonate **9** in a mixture of the alcohol (1 equiv.) in toluene with rhodium(II) acetate at 60°C resulted in the formation of the corresponding alkoxy compounds **26** in 45-87% yield (Scheme 3). With the more active rhodium(II) trifluoroacetamide the reaction proceeded at room temperature in slightly higher yield (63-94%). Surprisingly, these reactions were found to proceed faster with t-butanol than with methanol; this perhaps reflects the fact that methanol coordinates better with the metal centre making it a less effective catalyst.



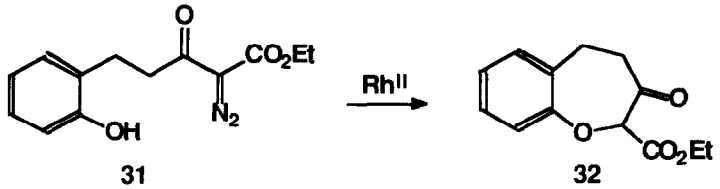
9

26a; R = Me,
26b; R = ^{i}Pr,
26c; R = ^{t}Bu

Scheme 3

However, when the reactions of the diazophosphonate **9** were carried out in equimolar mixtures of the alcohol and dichloromethane at room temperature with rhodium(II) trifluoroacetamide as catalyst, then very similar results to those described by Teyssié, albeit for a different diazo compound, were found. Thus based on the amount of each alkoxyphosphonate found by integration of the ^{1}H NMR spectra of the crude reaction mixtures, the relative reactivity of methanol: 2-propanol: t-butanol was found to be 2.0:1.1:1.0.

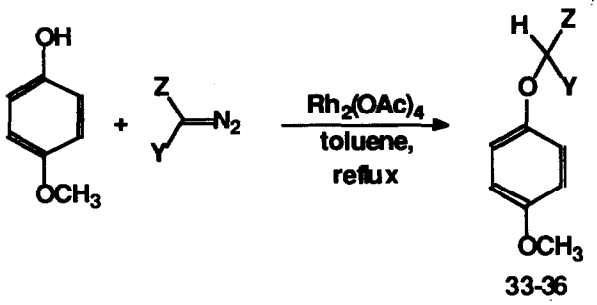
Insertion reactions into the O-H bonds of phenols were also investigated. We have already described an intramolecular version of this reaction,[22] cyclisation of **31** to give benzoxepane **32** (Scheme 4), and in parallel with our present work, another group has studied similar intermolecular reactions.[23]



31 **32**

Scheme 4

Thus various diazo compounds were decomposed using rhodium catalysts in the presence of 4-methoxyphenol in toluene. Perhaps not surprisingly, the α-diazo-bis phosphonate **11** failed to react even after 7 days at 110 °C in the presence of rhodium(II) acetate. However, the expected insertion products **33-36** were obtained in good yield (Table 3) from the diazo compounds **6**, **7**, **9**, and **10**.



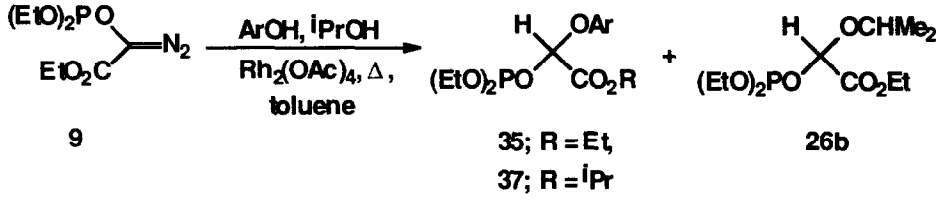
33-36

Table 3. The Reaction of Various Diazo Compounds with 4-Methoxyphenol

Diazo	Y	Z	Product	Yield (%)
6	CO_2Et	CO_2Et	**33**	73
7	$PhSO_2$	CO_2Et	**34**	70
9	$PO(OEt)_2$	CO_2Et	**35**	78
10	$PO(OEt)_2$	$PhSO_2$	**36**	81

The reaction of diethyl diazomalonate (**6**) with 4-methoxyphenol was repeated at room temperature using both rhodium(II) acetate and rhodium(II) trifluoroacetamide. When TLC showed complete consumption of **6**, the crude reaction mixture was analysed by ^1H NMR spectroscopy and by comparison with the spectra of the starting material and products and careful integration the ratios of the components of the mixtures could be determined. In the case of the rhodium(II) acetate catalysed reaction, 37% of the insertion product, 56% of the phenol and 6% of "reduced" product was observed. In the case of the rhodium(II) trifluoroacetamide catalysed reaction 45% of the insertion product, 50% of phenol and only 5% of "reduced" product were observed. It is clear that the best conditions for the preparation of products from the insertion reaction into phenols are those used initially (see Table 3), and that the reaction is synthetically useful.

Finally a comparison of the relative reactivity of alcohol and phenol O-H groups in rhodium mediated insertion reactions was undertaken since previous results suggested that 2-propanol (and alcohols in general) were more reactive towards the carbenoids than 4-methoxyphenol. We decided to confirm this by utilising the competition reaction shown in Scheme 5. The diazo substrate **9** was decomposed using rhodium(II) acetate in boiling toluene in the presence of 1 mole equiv. of each of 2-propanol and 4-methoxyphenol. The starting phenol was partially recovered (49%) along with the insertion products **26b** (derived from 2-propanol) and **35** (derived from 4-methoxyphenol)(63 and 23% respectively). Furthermore, a fourth compound was isolated (**37**, 15%) which was produced by the transesterification of **35** with 2-propanol. Thus, as expected, nucleophilic attack by the alcohol on the carbenoid is more efficient than that of the phenol.



9

35; R = Et,
37; R = ^{i}Pr

26b

Ar = 4-methoxyphenyl

Scheme 5

Effect of Catalyst

In further experiments we decided to extend our understanding of the effectiveness of various catalysts for such O-H insertion reactions. Three further catalysts were prepared; rhodium(II) trifluoroacetate $[Rh_2(tfa)_4]$,[24] rhodium(II) perfluorobutyrate $[Rh_2(pfb)_4]$[25] and rhodium(II) acetamide $[Rh_2(acm)_4]$,[26] and each compared with rhodium(II) acetate and trifluoroacetamide. Each of the diazo substrates **6**, **7**, **9**, **10** and **11** was treated with 2-propanol (1 equiv.) and each of the catalysts (1 mol%), individually. The reactions were carefully monitored by TLC and the time taken for all the diazo compound to be consumed was noted. After removal of the solvent the crude reaction mixtures were analysed by ^1H NMR which generally showed that the presence of both of O-H insertion product and "reduced" product. Comparison of the relative integration of relevant peaks allowed the ratio of products to be determined. The results of these experiments are detailed in Table 5. In the case of the diazo substrate **10**, the reaction was also attempted using two other catalysts. Rhodium(II) *N*-benzenesulfonyl-S-prolinate and rhodium(II) S-2-chloropropionate[27,28] were investigated. In each case only the reduced product $[PhSO_2CH_2PO(OEt)_2]$ was observed.

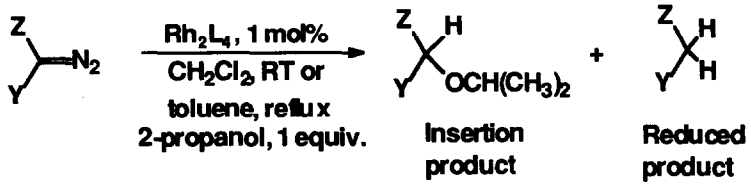
Some other trends are evident from Table 5. For a series of diazo compounds, the relative rate of decomposition is independent of the rhodium catalyst; *e.g.* the diazosulfone **7** generally decomposes faster than the diazophosphonate **9**. When rhodium carboxylates are used as the catalyst, then the rate of decomposition of a given diazo compound decreases as the ligand becomes more electron withdrawing; *e.g.* as the catalyst is changed from rhodium(II) acetate to trifluoroacetate to perfluorobutyrate, then the O-H insertion reactions tend to proceed slower. The most likely explanation of this catalyst effect is that the alcohol coordinates more strongly to the more electrophilic catalysts. If this complexation is too strong then the nucleophilic diazo carbon can interact less readily with the electrophilic catalyst, hence slowing its rate of decomposition. Thus for this group of 3 catalysts there is some correlation between the pKa of the ligand (pKa values in water: CH_3CO_2H = 4.76; CF_3CO_2H = 0.25; $C_3F_7CO_2H$ = 0.17) and catalytic activity. However, this correlation with ligand pKa does not hold completely since rhodium(II) trifluoroacetamide (ligand pKa = 10.36) is by far the most effective catalyst for O-H insertion reactions and therefore it is likely that other factors are important. In a recent communication, Pirrung suggested that the Rh-Rh bond length in the bridged dimeric species might have some effect on the catalytic activity of the rhodium(II) complex.[29] Some Rh-Rh bond distances relevant to this work are illustrated in Table 4.[10]

Table 4. Some Rh-Rh Bond Lengths

Bridging Ligand	Axial Ligand	r(Rh-Rh)/Å
CH_3CO_2	H_2O	2.385
	Pyridine	2.396
CH_3CONH	H_2O	2.415
CF_3CO_2	H_2O	2.409
	EtOH	2.396
CF_3CONH	Pyridine	2.472

Although initially it would seem that rhodium(II) trifluoroacetamide has the largest Rh-Rh bond of the complexes studied, no direct comparison using the published X-ray data is possible, since the Rh-Rh distance varies according to the nature of the axial ligand.

In a related study Hubert and co-workers[30] concluded that solubility of the catalyst was one of the major considerations in the effectiveness of rhodium catalysts. We consider this to be unlikely in our case, since although no detailed studies of the solubility of these catalysts was undertaken, it was clear that rhodium(II) trifluoroacetamide was the *least* soluble of all the catalysts in either dichloromethane or toluene but it gave the best results.



6, Y = Z = CO_2Et
7, Y = $PhSO_2$, X = CO_2Et
9, Y = $PO(OEt)_2$, X = CO_2Et
10, Y = $PhSO_2$, X = $PO(OEt)_2$
11, Y = Z = $PO(OEt)_2$

Table 5. The Effect of Catalyst Ligand in the Rhodium Carbenoid Mediated Insertion into 2-Propanol

Catalyst	Diazo	Time (h)	Temp (°C)	Ratio of Products Insertion : Reduction	
$Rh_2(OCOCH_3)_4$	**6**	62	RT	97	3
	7	45	RT	60	40
	9	6	110	95	5
	10	NR	-	-	-
	11	NR	-	-	-
$Rh_2(OCOCF_3)_4$	**6**	65	RT	76	24
	7	180	RT	77	33
	9	2.5	110	88	12
	10	6	110	35	65
	11	300	110	69	31
$Rh_2(OCOC_3F_7)_4$	**6**	520	RT	63	37
	7	1.0	110	74	26
	9	1.75	110	100	0
	10	116	110	13	87
	11	NR	-	-	-
$Rh_2(NHCOCH_3)_4$	**6**	44	RT	86	14
	7	132	RT	73	27
	9	20	110	88	12
	10	48	110	39	61
	11	20	110	91	9
$Rh_2(NHCOCF_3)_4$	**6**	0.06	RT	86	14
	7	0.4	RT	100	0
	9	50	RT	71	29
	10	15	110	81%[a]	-
	11	6	110	75%[a]	-

Notes. [a] isolated yield. [NR = no reaction].

Origin of the "Reduced" Product

The (re)formation of the methylene compound from the diazo compound has proven to be a common side reaction in the rhodium catalysed insertion reactions described (Table 5). Strausz and co-workers, have described the formation of acetone in the photochemical reaction of ethyl diazoacetate with 2-propanol,[31] and we have now confirmed that this is also the case in rhodium mediated processes. Thus dimethyl diazomalonate was decomp-osed in the presence of carefully purified 2-propanol and rhodium(II) trifluoroacetate in $CDCl_3$, and the reaction followed by ^1H NMR spectroscopy. Analysis of the spectra indicated the formation of acetone along with the insertion product dimethyl isopropyloxymalonate[32] and the reduced product, dimethyl malonate, although the analysis was complicated by the presence of other (unidentified) compounds. The simplest explanation for the formation of the "reduced" product is hydrogen abstraction from 2-propanol by the rhodium carbenoid. However, the operation of alternative catalytic cycles involving a rhodium hydride, formed by oxidation of the alcohol by rhodium(II) [or by any rhodium(III) formed by disproportionation], cannot be discounted.[33]

Conclusions

We have described a range of rhodium carbenoid mediated O-H insertion reactions using variations in both catalyst and diazo substrates. It is clear that α-diazophosphonates are markedly less prone to such reactions than the corresponding α-diazo sulfones and carbonyl compounds, although this can be overcome by using a more active catalyst such as rhodium(II) trifluoroacetamide. The reactions are synthetically useful, and can be extended to other hydroxylic compounds such as phenols.

EXPERIMENTAL

General Experimental Details

Commercially available solvents and reagents were used without further purification, except for those detailed below which were purified as described. 'Light petroleum' refers to the fraction boiling between 40 and 60 °C, and was distilled from calcium chloride before use, as was ethyl acetate. Dichloromethane was distilled from phosphorus pentoxide. 'Ether' refers to diethyl ether, this was also routinely distilled from calcium chloride. All of the above distillations employed a 36 cm Vigreux column. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under nitrogen prior to use. In the case of the experiment which aimed to determine the origin of the reduced product the 2-propanol was distilled from 2,4-dinitrophenylhydrazine.

TLC analyses were carried out using Merck Kieselgel 60 F_{254} silica plates. All compounds subjected to other analyses were chromatographically homogeneous. Liquids were distilled using the "bulb-to-bulb" technique on a Büchi GKR-51 apparatus and the boiling points quoted refer to the temperature of the oven. Melting points were carried out using an Electrothermal Digital Melting Point instrument and are uncorrected. ^1H NMR and ^{13}C NMR spectroscopy were carried out using a Bruker AC 250 instrument at 250 and 62.9 MHz respectively as solutions in deuteriochloroform unless stated otherwise. Diazo carbons were often not observed due to their long relaxation time. The chemical shifts of the signals quoted are in parts per million (p.p.m.) in relation to the $CDCl_3$ peak set at δ 7.265. Infra-red (IR) spectra were recorded on a Nicolet 205 FT-IR instrument as liquid films between two NaCl discs unless stated otherwise. Elemental analyses were carried out using a Perkin Elmer Elemental Analyser 2450 CHN instrument and mass spectral data were recorded either in Loughborough on a Kratos MS80 or using the S.E.R.C. Mass Spectrometry Service based at Swansea.

The preparations of the diazo compounds described within this paper have been reported previously. In particular, we have already described the preparation triethyl diazophosphonoacetate **9** and the product **26b** of its rhodium mediated insertion reaction into 2-propanol.[6a] Descriptions of the preparations of ethyl *N,N*-dimethylcarbamoyl diazoacetate **4** and bis-(phenylsulfonyl) diazomethane **13** are given later (this compound has

been prepared previously using a different method). All diazo transfer reagents were prepared according to literature methods.

Ethyl N,N-dimethylcarbamoyl diazoacetate **4**.
Dimethylamine (excess) was added to a mixture of the diazo acid chloride **14** (5.30 g, 30 mmol), triethylamine (3.03 g, 30 mmol) in dry dichloromethane (50 ml) and the mixture was allowed to stir at room temperature. When the reaction was complete (TLC) the mixture was washed with water (3 x 50 ml), dried ($MgSO_4$) and the solvent was removed *in vacuo*. The residue was then chromatographed on silica to afford the homogeneous diazo compound as a yellow oil (4.17 g, 75 %), (Found: M+H$^+$, 186.0879. $C_7H_{11}N_3O_3$+H requires 186.0879);$\nu_{max.}$ (film)/cm^{-1} 2982, 2962, 2935, 2127, 1713, 1632 and 1240; δ_H 1.31 (3 H, t, $OCH_2\mathit{Me}$, J 7.1), 3.01 (6 H, s, NMe_2), and 4.25 (2 H, q, $OC\mathit{H}_2Me$, J 7.1); δ_C 14.41 ($OCH_2\mathit{Me}$), 37.80 (br, NMe_2), 61.34 (OCH_2Me), 161.73 and 162.94 (2 x C=O); *m/z* (CI) 186 (100%), 175 (26), 158 (16), 114 (38) and 46 (15).

bis-(Phenylsulfonyl) diazomethane **13**.
A solution of commercially available bis-(phenylsulfonyl) methane (1.48 g, 5 mmol) in freshly distilled THF (25 ml) was added via a syringe to a stirred suspension of sodium hydride (0.125 g, 5 mmol) in freshly distilled THF (25 ml) under an atmosphere of dry nitrogen. After *ca.* 15 min a further portion of THF (50 ml) was added to keep the reaction mixture stirring freely. The whole was allowed to stir at room temperature for 1 h before a solution of tosyl azide (0.99 g, 5 mmol) in dry THF (25 ml) was added via a syringe. The reaction mixture was left to stir for 16 h under an inert atmosphere at room temperature. Water (100 ml) and ether (100 ml) were added and the organic layer was separated before the aqueous layer was extracted with ether (4 x 75 ml). The combined organic extracts were washed with water (12 x 100 ml) until the aqueous layer remained colourless and the resulting solution was dried ($MgSO_4$). The solvent was removed *in vacuo* and the residue was chromatographed on silica (1:1 light petroleum-ether) to afford the title compound (1.01 g, 3.13 mmol; 62%) as a yellow crystalline solid, m.p. 97-98 °C (decomp. gaseous evolution; lit.,[18] 99-100 °C).

General Procedure for the Rhodium(II) Catalysed Intermolecular O-H Insertion reactions of 2-Propanol.

The appropriate diazo compound (1.0 mmol) was added to a suspension of rhodium (II) acetate (4.4 mg, 0.01 mmol) in a mixture of dichloromethane (2 ml) and 2-propanol (9.19 ml, 7.2 g, 0.12 mol). The reaction was stirred at room temperature until complete (as determined by TLC). The volatiles were removed by evaporation and the residue chromatographed on silica to yield the respective insertion product. In the case of the various phosphonates where the reaction was very slow, the reaction mixture was heated to reflux temperature.

Ethyl 2-isopropyloxyacetate **18**.
(64%), (Found: M+H$^+$, 147.1021. $C_7H_{14}O_3$+H requires 147.1021); $\nu_{max.}$(film)/cm^{-1} 2972, 2936, 1756, 1380, 1370, 1278, 1204, 1126 and 1034; δ_H 1.20 (6 H, d, J 6.1, Me_2CH), 1.29 (3 H, t, J 7.1, $OCH_2\mathit{Me}$), 3.68 (1 H, h, J 6.1, $Me_2C\mathit{H}$), 4.07 (2 H, s, CH_2) and 4.23 (2 H, q, J 7.1, $OC\mathit{H}_2Me$); δ_C 14.25 ($OCH_2\mathit{Me}$), 21.83 ($OCH\mathit{Me}_2$), 60.70 (OCH_2Me), 65.85 (OCH_2), 72.59 ($OCHMe_2$) and 170.934 (C=O); *m/z* (EI$^+$) 127 (8%), 99 (26), 88 (7), 73 (25) and 43 (100).

Ethyl 2-isopropyloxyphenylacetate **19**.
(92%), (Found: M+H$^+$, 223.1334. $C_{13}H_{18}O_3$+H requires 223.1334); $\nu_{max.}$ (film)/cm^{-1} 2976, 1751, 1732 and 1203; δ_H 1.20 (9H, m, Me_2CH and $\mathit{Me}CH_2O$), 3.71 (1 H, h, $C\mathit{H}Me_2$), 4.16 (2 H, q, $OC\mathit{H}_2CH_3$), 4.97 (1 H, s, $C_6H_5C\mathit{H}$-O), and 7.26-7.49 (5 H, m, C_6H_5); δ_C 14.00 ($OCH_2\mathit{Me}$), 22.00 (2 C, $CH\mathit{Me}_2$), 61.00 ($\mathit{C}HMe_2$),

70.85 (2 C, O*C*H_2Me), 78.46 (C_6H_5*C*H-O), 127.02 (C_6H_5), 128.29 (C_6H_5), 128.41 (C_6H_5), 137.27 (C_6H_5) and 171.48 (C=O); *m/z* (CI^+) 198 (12), 196 (10), 181 (18), 180 (71), 163 (15), 149 (26) and 105 (8).

Ethyl 2-isopropyloxy-3-phenylpropanoate **20**.
(32%), (Found: M+H^+, 237.1490. $C_{14}H_{21}O_3$+H requires 237.1491); $\nu_{max.}$ (film)/cm^{-1} 2976, 2934, 1748, 734 and 699; δ_H 0.94 (3 H, d, *J* 6.1, *Me*$_2$CH), 1.15 (3 H, d, *J* 6.1, *Me*$_2$CH), 1.23 (3 H, t, *J* 7.1, OCH$_2$*Me*), 2.89-3.05 (2 H, m, PhC*H*$_2$), 3.50 (1 H, h, *J* 6.1, OC*H*Me$_2$), 4.02-4.08 (1 H, m, OCH), 4.13-4.22 (2 H, m, OC*H*$_2$Me) and 7.24-7.26 (5 H, m, C_6H_5); δ_C 14.1 (*Me*CH$_2$O), 21.2 (*Me*$_2$CH), 22.5 (*Me*$_2$CH), 39.6 (PhCH$_2$), 60.7 (OCHMe$_2$), 72.3 (OCH$_2$Me), 78.2 (OCH), 126.4 (C_6H_5), 128.0 (C_6H_5), 128.4 (C_6H_5), 137.3 (C_6H_5) and 173.0 (*C*=O); *m/z* (CI) 237 (MH+) (50), 195 (90), 163 (85) and 91 (100).

Ethyl 2-(N,N-dimethylcarbamoyl)-2-isopropyloxyacetate **21**.
(66%), b.p. 125 °C at 3 mmHg, (Found: *M*+H^+ 218.1392. $C_{10}H_{19}NO_4$ + H requires 218.1392); $\nu_{max.}$ (film)/cm^{-1} 2937, 1757 and 1656; δ_H 1.21-1.39 (9 H, m, *Me*$_2$CH and *Me*CH$_2$O), 2.95, 3.06 (each 3 H, s, NMe$_2$), 3.76 (1 H, h, C*H*Me$_2$), 4.20 (2 H, m, OC*H*$_2$CH$_3$), and 4.75 (1 H, s, CH-O); δ_C 14.07 (OCH$_2$*Me*), 21.70, 21.94 (CH*Me*$_2$), 36.00, 36.83 (NMe$_2$), 61.56 (*C*HMe$_2$), 72.72 (OCH$_2$Me), 78.61 (CH-O), 166.58 and 168.40 (2 x C=0); *m/z* (EI^+) 202 (22), 176 (27), 159 (10), 130 (4), 102 (18) and 72 (100).

Ethyl 2-cyano-2-isopropyloxyacetate **22**.
(86%), (Found: *M*+H^+, 172.0970. $C_8H_{13}O_3N$+H requires 172.0974); $\nu_{max.}$ (film)/cm^{-1} 2983, 1770, 1751, 1299, 1284, 1213, 1183, 1142, 1114 and 1025; δ_H 1.23-1.38 (9 H, m, OCH$_2$*Me* and CH*Me*$_2$), 3.97 (1 H, h, *J* 6.1, C*H*Me$_2$), 4.34 (2 H, q, *J* 7.2, OC*H*$_2$Me) and 4.81 (1 H, s, OCH); δ_C 13.96 (OCH$_2$*Me*), 21.32 (OCH*Me*$_2$), 22.14 (OCH*Me*$_2$), 63.34 (OCH$_2$Me), 65.61 (OCH), 74.22 (OCHMe)$_2$, 114.71 (C≡N) and 163.79 (C=O); *m/z* (CI^+) 189 (*M*+NH_4^+, 100%), 172 (*M*H^+, 10), 118 (1), 102 (4), 85 (5) and 49 (27).

Diethyl 2-isopropyloxymalonate **23**.
(66%), (Found: *M*+NH_4^+, 236.1498. $C_{10}H_{18}O_5$+NH_4 requires 236.1498); $\nu_{max.}$ (film)/cm^{-1} 2980, 2936, 1764, 1740, 1466, 1384, 1370, 1322, 1224, 1180 and 1032; δ_H 1.24-1.33 (12 H, m, 2 x OCH$_2$*Me* and *Me*$_2$CH), 3.77 (1 H, h, *J* 6.2, Me$_2$C*H*), 4.20-4.31 (4 H, m, OC*H*$_2$Me) and 4.54 (1 H, s, OCH); δ_C 14.07 (OCH$_2$*Me*), 21.91 (OCH*Me*$_2$), 61.64 (OCH$_2$Me), 73.39 (OCHMe$_2$), 77.25 (COCH) and 167.24 (C=O); *m/z* (CI^+) 236 (*M*+NH_4^+, 100%), 219 (*M*H^+, 25), 194 (44), 177 (22) and 161 (35).

Ethyl 2-benzenesulfonyl-2-isopropyloxyacetate **24**.
(64%), (Found: *M*+NH_4^+, 304.1219. $C_{13}H_{18}O_5S$+NH_4 requires 304.1219); $\nu_{max.}$ (film)/cm^{-1} 2980, 1746, 1326, 1310, 1232, 1186, 1154, 1108, 1080 and 688; δ_H 1.15-1.32 (9 H, m, OCH$_2$*Me* and *Me*$_2$CH), 3.99 (1 H, h, *J* 6.1, Me$_2$C*H*), 4.23 (2 H, q, *J* 7.1, OC*H*$_2$Me), 4.94 (1 H, s, OC*H*) and 7.53-7.93 (5 H, m, C_6H_5S); δ_C 13.94 (OCH$_2$*Me*), 21.41 (OCH*Me*$_2$), 22.04 (OCH*Me*$_2$), 62.65 (OCH$_2$Me), 76.85 (OCH), 92.47 (OCH), 128.85 (C_6H_5), 129.96 (C_6H_5), 134.44 (C_6H_5), 135.80 (C_6H_5) and 164.30 (C=O); *m/z* (EI^+) 287 (*M*H^+-OC_3H_7, 16%),185 (76), 143 (40), 125 (37), 103 (100), 78 (53) and 43 (65).

Ethyl 2-isopropyloxy-2-diphenylphosphinyl diazoacetate **25**.
A mixture of the diazo compound **8** (200 mg, 0.64 mmol), 2-propanol (216 mg, 3.2 mmol) and rhodium (II) trifluoroacetamide (5 mg) in toluene (25 ml) was stirred for 2 h at room temperature. The solvent was removed by evaporation and the residue chromatographed on silica (ether-light petroleum) to yield the *title compound* (99 mg, 45%), m.p. 85-86°C (from light petroleum-ether), (Found: *M*+H^+, 347.1412. $C_{19}H_{23}O_4P$+H requires 347.1412); $\nu_{max.}$ (nujol mull)/cm^{-1} 2956, 2871, 1750, 1228, 1119, 1100, 726 and 699; δ_H 0.86 (6 H, d, *J* 7.6, *Me*$_2$CH), 1.05 (3 H, t, *J* 7.1, OCH$_2$*Me*), 3.51 (1 H, h, *J* 7.6, OC*H*Me), 4.06 (2 H, q, J 7.1, OC*H*$_2$Me), 4.71

(1 H, d, $J_{H,P}$ 16.0, OCHP),7.42-7.51 (6 H, m, C_6H_5) and 7.80-8.01 (4 H, m, C_6H_5); δ_C 13.86 (Me_2CH), 20.71 (OCH_2Me), 61.57 (OCHMe), 78.11 (d, $J_{C,P}$73.8, OCHP),127.99, 128.06, 128.17, 128.26, 131.90, 132.00, 132.07, 132.20 (aromatics) and 168.29 (C=O); *m/z* (EI^+) 347 (18), 346 (2), 219 (50), 201 (100), 77 (44) and 47 (34).

Ethyl 2-isopropyloxy-2-diethyl phosphonoacetate **26b**.
Prepared as previously described.[6a]

Diethyl 1-(isopropyloxy)-1-phenylsulfonylmethane phosphonate **27**.
A mixture of benzenesulfonyl-diethyl phosphono-diazomethane **10** (0.50 g, 1.57 mmol), 2-propanol (0.6 ml, 0.47 g, 7.86 mmol) and rhodium (II) acetate (6.9 mg, 0.016 mmol) in toluene (30 ml) was refluxed for 72 h. The solvent was removed by evaporation and the residue chromatographed on silica (ether-ethyl acetate) to yield the *title compound* as a colourless oil (0.37 g, 67%), (Found: M+NH_4^+, 368.1300. $C_{14}H_{23}O_6PS$+NH_4 requires 368.1297); $\nu_{max.}$ (film)/cm^{-1} 1322, 1311, 1260, 1157, 1142, 1098, 1073, 1050 and 1024; δ_H 1.14-1.37 (12 H, m, $OCHMe_2$ and 2 x OCH_2Me), 4.03-4.25 (5 H, m, $OCHMe_2$ and OCH_2Me), 4.73 (1 H, d, J 12.5, OCHP) and 7.52-8.04 (5 H, m, C_6H_5); δ_C 16.28 (2 C, m, OCH_2Me), 21.27 ($OCHMe_2$), 22.15 ($OCHMe_2$), 64.09 (d, OCH_2Me), 77.89 (d, J 6.0, $OCHMe_2$), 90.34 (d, J 169.2, OCHP), 128.61 (C_6H_5), 130.21 (C_6H_5), 134.20 (C_6H_5) and 137.02 (C_6H_5); *m/z* (CI^+) 368 (M+NH_4^+), 351 (MH^+, 6), 228 (44), 211 (7), 184 (19), 170 (4) and 156 (16).

Diethyl 1-(isopropyloxy)-1-diethyl phosphonomethane phosphonate **28**.
A mixture of diethyl phosphono-diethyl phosphono-diazomethane [bis-(diethyl phosphono)-diazomethane) **11** (1.0 g, 3.18 mmol), 2-propanol (1.22 ml, 0.96 g, 0.016 mol) and rhodium (II) trifluoroacetamide (21 mg, 0.032 mmol) was refluxed for 2 h in dry toluene (60 ml). The solvent was removed by evaporation and the residue chromatographed on silica (dichloromethane-methanol) to yield the *title compound* (0.89 g, 81%), b.p. 160°C at 4 mmHg, (Found: M+H^+, 347.1390. $C_{12}H_{28}O_7P_2$+H requires 347.1389); $\nu_{max.}$ (film)/cm^{-1} 2981, 1255, 1165, 1097, 1049, 1026 and 975; δ_H 1.21 (6 H, d, J 6.1, $CHMe_2$), 1.35 (6 H, t, J 7.1, 2 x OCH_2Me), 1.36 (6 H, t, J 7.1, OCH_2Me), 3.98 (1 H, h, J 6.1, $CHMe_2$), 4.07 (1 H, t, J 17.7, OCHP) and 4.18-4.30 (8 H, m, OCH_2Me); δ_C 16.50, 16.54 ($OCHMe_2$), 21.77 (OCH_2Me), 63.22, 63.27, 63.32, 63.37 (4 x OCH_2Me), 70.86 (t, J 158.5, PCHP), and 75.61 ($OCHMe_2$); *m/z* (CI^+) 347 (MH^+, 100%), 319 (3), 305 (3), 288 (6), 261 (3), 167 (8) and 152 (3).

General Procedure for Photolysis Experiments

A solution of diethyl phenylsulfonyl(diazomethyl)phosphonate **10** (0.15 g, 0.47 mmol) in the dry alcohol (10 ml), in a quartz test-tube, was deoxygenated and simultaneously put under an atmosphere of nitrogen by bubbling nitrogen through it, *via* a syringe needle, for 30 min. The reaction was irradiated for varying periods of time with a medium pressure mercury vapour lamp. When the reaction was complete (as determined by TLC), the solvent was removed by evaporation and the residue chromatographed on silica (ether-ethyl acetate) to yield the insertion products as clear oils.

Diethyl 1-methoxy-1-phenylsulfonylmethanephosphonate **29a**.
(63%), (Found: M+H^+, 323.0718. $C_{12}H_{19}O_6PS$+H requires 323.0718); $\nu_{max.}$ (film)/cm^{-1} 1446, 1324, 1312, 1264, 1158, 1102, 1078, 1046, 980, 732 and 688; δ_H 1.21-1.37 (6 H, m, 2 x OCH_2Me), 3.68 (3 H, s, OMe), 4.07-4.21 (4 H, m, 2 x OCH_2Me), 4.53 (1 H, d, J 12.6, SCHP) and 7.36-8.02 (5 H, m, C_6H_5S); δ_C 13.90 (OCH_2Me), 61.39 (OMe), 62.75 (OCH_2Me), 95.78 (OCH), 129.00 (C_6H_5), 129.75 (C_6H_5), 134.59 (C_6H_5),

135.64 (C_6H_5) and 165.42 (C=O); *m/z* (EI$^+$) 323 (*M*H$^+$, 42%), 291 (5), 182 (5), 121 (100), 91 (5), 77 (23), 51 (11) and 29 (5).

Diethyl 1-(t-butyloxy)-1-phenylsulfonylmethanephosphonate **29b**.
(44%), (Found: *M*+H$^+$, 365.1188. $C_{15}H_{25}O_6SP$+H requires 365.1188); $\nu_{max.}$ (film)/cm^{-1} 2980, 1370, 1322, 1310, 1260, 1174, 1158, 1092, 1070, 1052, 1024, 978 and 688; δ_H 1.15-1.39 (15 H, m, 2 x OCH_2*Me* and t-Bu), 4.03-4.20 (4 H, m, 2 x OCH_2Me), 4.95 (1 H, d, *J* 11.2, SC*H*P) and 7.51-8.01 (5 H, m, C_6H_5S); δ_C 13.98 (OCH_2*Me*), 27.32 (t-Bu), 62.57 (OCH_2Me), 79.54 ($OCMe_3$), 88.02 (OCH), 128.70 (C_6H_5), 130.25 (C_6H_5), 134.37 (C_6H_5),135.89 (C_6H_5) 165.53 (C=O); *m/z* (EI$^+$) 365 (*M*H$^+$, 6%), 309 (10), 167 (100), 139 (23), 111 (23), 77(13), 57 (17) and 41 (11).

2-Benzenesulfonyl-2-methoxy styrene **30**.
A solution of diethyl 1-methoxy-1-phenylsulfonylmethanephosphonate **29a** (0.1 g, 0.31 mmol) in THF (2 ml) was added dropwise to a suspension of sodium hydride (80%, 10 mg, 0.34 mmol) in THF (15 ml) at 0 °C. After stirring the reaction for 30 min, a solution of benzaldehyde (33 mg, 0.31 mmol) in THF (1 ml) was added. The reaction was then allowed to stir overnight at room temperature. Ether (20 ml) and water (20 ml) were added and the aqueous layer extracted with ether (3 x 20 ml). The combined ethereal extracts were washed with brine (20 ml) and dried ($MgSO_4$). The solvent was removed by evaporation and the residue chromatographed on silica (light petroleum-ether) to yield the *title compound* (48 mg, 0.175 mmol, 56%, E:Z *ca.* 95:5), (Found: *M*$^+$, 274.0664. $C_{15}H_{14}O_3S$ requires 274.0664); $\nu_{max.}$ (CCl_4)/cm^{-1} 1446, 1348, 1322, 1308, 1158, 1094, 1062, 718, 688 and 616; δ_H 3.67 (3 H, s, O*Me*) and 7.23-7.55 (11 H, m, C_6H_5S, C_6H_5C and CH); *m/z* (EI$^+$) 274 (*M*$^+$, 34%), 149 (16), 118 (100), 90 (42), 71 (17) and 51 (12).

Ethyl 2-Isomethoxy-2-diethyl phosphonacetate ***26a***.
A mixture of triethyl diazophosphonoacetate (250 mg, 1 mmol) and rhodium trifluoroacetamide (6 mg, 1 mol%) was taken up into methanol (10 ml, excess) and allowed to stir at room temperature. When TLC indicated complete consumption of the diazo starting material then the solvent was removed *in vacuo* and the residue was chromatographed on silica (ether-ethyl acetate) to yield the title compound as a colourless oil (244 mg, 94%). (Found: M+H$^+$ 255.0998. $C_9H_{19}O_6P$+H requires 255.0998); $\nu_{max.}$ (film)/cm^{-1} 2937, 1750, 1261 and 1026; δ_H 1.24-1.37 (9H, m, 3 x OCH_2*Me*), 3.62 (3 H, s, OMe), and 4.16-4.39 (7H, m, 3xOCH_2Me and OCHP); δ_C 14.00 (CO_2CH_2*Me*), 16.16, 16.26 {PO(OCH_2Me)$_2$}, 60.37 (OMe), 61.69 (OCH_2Me), 63.50, 63.66 {PO(OCH_2Me)$_2$}, 78.51 (d, *J* 153.8, OCHP) and 167.05 (C=O); *m/z* (EI$^+$) 255 (8), 224 (11), 197 (32), 155 (34), 121 (51) and 65 (100).

Ethyl 2-t-butyloxy-2-diethyl phosphonacetate **26c**.
(63%), (Found: *M*+H$^+$, 297.1467. $C_{12}H_{25}O_6P$+H requires 297.1467); $\nu_{max.}$ (film)/cm^{-1} 2980, 1752, 1256, 1184, 1164, 1100, 1050, 1028 and 976; δ_H 1.20-1.38 (18 H, m, t-Bu and 3 x OCH_2*Me*), 4.20-4.28 (6 H, m, OCH_2Me) and 4.45 (1 H, d, *J* 21.0, OCHP); δ_C 14.10 (OCH_2*Me*), 16.37 (OCH_2*Me*), 16.47 (OCH_2*Me*), 27.31 (t-Bu), 61.60 (OCH_2Me), 63.70 (2 C, m, OCH_2Me), 70.09 (d, *J* 159.7, OCHP), 77.67 ($OCMe_3$) and 169.32 (d, *J* 3.9, C=O); *m/z* (EI$^+$) 297 (*M*H$^+$, 21%), 241 (100), 194 (5), 167 (24), 138 (21), 111 (13), 57 (11) and 29 (9).

General procedure for the Competition Reactions of Alcohols with Triethyl Diazophosphonoacetate 9.

The two alcohols (each 1 mmol) were added to a mixture of the diazo compound **9** (250 mg, 1 mmol) and rhodium trifluoroacetate (5.6 mg, 0.01 mmol, 1 mol%) in dichloromethane (25 ml). The reaction was allowed to stir at room temperature for *ca.* 50 h after which time TLC indicated total consumption of the starting diazo compound. The solvent was removed *in vacuo* and the residue was examined by ^{1}H NMR spectroscopy to determine the ratio of insertion products by comparison with the spectra of the authentic materials.

General Procedure for the Rhodium(II) Mediated Insertion Reactions into 4-Methoxyphenol

A mixture of the desired diazo compound (2 mmol), 4-methoxyphenol (248 mg, 2 mmol), rhodium(II) acetate (27 mg, 6 x 10^{-5} mol, 3 mol%) and dry toluene (25 ml) was heated under reflux for 40 h. After this time TLC indicated complete conversion of the diazo compound [which was confirmed by the lack of a diazo absorption (*ca.* 2140 cm^{-1}) in the IR spectrum of the crude reaction mixture]. The solvent was removed *in vacuo* and the residue was chromatographed.

Diethyl 2-(4-methoxyphenoxy)malonate **33**.
The eluent used for column chromatography was light petroleum-ether (1:1); (73%), b.p. 180 °C at 2.0 mmHg. (Found M^+, 282.1103 $C_{14}H_{18}O_6$ requires 282.1103); $\nu_{max.}$ (film)/cm^{-1} 2992, 1747, 1739, 1508, 1466, 1371, 1240, 1112, 1099 and 829; δ_H 1.29 (6 H, t, 2 x $OCH_2\mathit{Me}$, *J* 7.1), 3.76 (3 H, s, ArO*Me*), 4.29 (4 H, q, 2 x $OC\mathit{H}_2$Me, *J* 7.1), 5.09 (1 H, s, O*CH*), 6.81 (2 H, m, C_6H_5) and 6.94 (2 H, m, C_6H_5); δ_C 14.02 ($OCH_2\mathit{Me}$), 55.65 (ArO*Me*), 62.37 (OCH_2Me), 78.18 (OCH), 114.75 (C_6H_4), 117.15 (C_6H_4), 128.13 (C_6H_4), 129.50 (C_6H_4) and 165.81 (2 x C=O); *m/z* (EI) 237 (M^+) (5), 209 (11), 163 (15), 123 (100).

Ethyl 2-benzenesulfonyl 2-(4-methoxyphenoxy)acetate **34**.
The eluent used for the column chromatography was light petroleum-ether (1:1); (70%), b.p. 225 °C at 1.0 mmHg. (Found C, 58.25; H, 4.90. $C_{17}H_{18}O_6S$ requires C, 58.3; H, 5.15%) (Found: $M+NH_4^+$, 368.1168 $C_{17}H_{18}O_6S+NH_4$ requires 368.1168); δ_H 1.29 (3 H, t, $OCH_2\mathit{Me}$, *J* 7.1), 3.75 (3 H, s, ArO*Me*), 4.28 (2 H, q, $OC\mathit{H}_2$Me, *J* 7.1), 5.43 (1 H, s, OCH), 6.79 (4 H, m, C_6H_4), 7.57 (2 H, m, C_6H_5), 7.67 (1 H, m, C_6H_5) and 7.99 (2 H, m, C_6H_5); δ_C 13.97 ($OCH_2\mathit{Me}$), 55.65 (ArO*Me*), 63.09 (OCH_2Me), 93.28 (OCH), 114.82, 118.09, 129.04, 130.08, 134.74, 135.90, 151.50, 157.51 (aromatics) and 163.36 (C=O); *m/z* (EI^+) 304 (37), 290 (41), 228 (26), 137 (65).

Ethyl 2-(4-methoxyphenoxy)-2-diethyl phosphonoacetate **35**.
The eluent used for the column chromatography was light petroleum-ether (1:1) with gradual increase in the polarity of the eluent to a mixture of ethyl acetate-light petroleum (1:10); (78%), b.p. 185 °C at 0.4 mmHg. (Found: 346.1181. $C_{15}H_{23}O_7P$ requires 346.1181); $\nu_{max.}$(film)/cm^{-1} 2915, 2920, 1752, 1262, 1182, 1023 and 827; δ_H 1.29 (9 H, m, 3 x $OCH_2\mathit{Me}$), 3.78 (3 H, s, ArO*Me*), 4.27 (6 H, m, 3 x $OC\mathit{H}_2$Me), 4.93 (1 H, d, POC*H*, *J* 18.9), 6.29 (2 H, m, C_6H_5) and 6.88 (2 H, m, C_6H_5); δ_C 13.98 ($CO_2CH_2\mathit{Me}$), 16.27, 16.36 [PO($OCH_2\mathit{Me}$)], 55.56 (ArO*Me*), 62.06 (CO_2CH_2Me), 64.01, 64.06 [PO(OCH_2Me)], 75.51 (d, POCH, *J* 156.37), 114.60 (C_6H_4), 116.57 (C_6H_4), 152.50 (C_6H_4), 155.06 (C_6H_4) and 166.62 (*C*=O); *m/z* (EI) 346 (M^+) (63), 273 (12) and 123 (100).

Diethyl 1-(4-methoxyphenoxy)-1-phenylsulfonylmethane phosphonate **36**.
The eluent used for column chromatography was light petroleum-ether (1:1) with gradual increase in the polarity of the eluent to a mixture of ethyl acetate-light petroleum (1:10); (81%), b.p. 180 °C at 2.0 mmHg. (Found

414.0902. $C_{18}H_{23}O_7SP$ requires 414.0902); $\nu_{max.}$ (film)/cm^{-1} 2985, 1753, 1447, 1331, 1262, 1161, 1026 and 829; δ_H 1.31 (6 H, m, 2 x OCH_2Me), 3.76 (3 H, s, ArO*Me*), 4.27 (4 H, m, 2 x OCH_2Me), 4.93 (1 H, d, POCH, *J* 18.7), 6.75 (2 H, m, C_6H_5), 6.88 (2 H, m, C_6H_5), 7.56 (2 H, m, C_6H_5) and 9.96 (2 H, m, C_6H_5); δ_C 16.36, 16.45 [$PO(OCH_2Me)_2$], 55.67 (ArO*Me*), 64.58, 64.68 [$PO(OCH_2Me)$], 75.85 (d, POCH, *J* 150.64), 114.75, 116.06, 116.75, 118.39, 128.81, 129.23, 129.72, 130.26 and 134.42 (aromatics); *m/z* (EI) 414 (8), 346 (100), 273 (24), 218 (22), 167 (46), and 124 (100).

Competition Reaction of an Alcohol and a Phenol with Triethyl Diazophosphonoacetate 9.
Rhodium acetate (11 mg, 1 mol%) was added to a mixture of triethyl diazophosphonoacetate (626 mg, 2.5 mmol), 4-methoxyphenol (310 mg, 2.5 mmol), 2-propanol (150 mg, 2.5 mmol) and toluene (30 ml). The mixture was heated under reflux until TLC indicated the complete consumption of the diazo compound (*ca.* 45 h). The solvent was removed *in vacuo* and the residue was chromatographed. 4-Methoxyphenol (153 mg, 49%) was recovered along with the product of insertion into 2-propanol (**26b**) (444 mg, 1.58 mmol, 63%), the product of insertion into the phenol (**35**) (199 mg, 0.575 mmol, 23%) and the product of transesterification of **35**, (**37**) (135 mg, 0.375 mmol, 15%).

Isopropyl 1-(4-methoxyphenoxy)-1-diethyl phosphonoacetate 37
(15%) (Found: *M*+H$^+$ 361.1416. $C_{16}H_{25}O_7P$+H$^+$ requires 361.1416); $\nu_{max.}$ (film)/cm^{-1} 2983, 1749, 1260 and 1024; δ_H 1.23 (3 H, d, *Me*CH, *J* 6.3), 1.26 (3 H, d, *Me*CH, *J* 6.3), 1.37 (6 H, t, 2 x OCH_2Me, *J* 7.0), 3.75 (3 H, s, ArO*Me*), 4.26, (4 H, m, 2 x OCH_2Me), 4.91 (1 H, d, OC*H*P, $J_{H,P}$ 18.73), 5.14 (1 H, h, $OCHMe_2$, *J* 6.3) and 6.71-6.84 (4 H, m, C_6H_4); δ_C 15.35, 15.44 ($CHMe_2$), 20.46, 20.69 [$PO(OCH_2Me)_2$], 54.64 (ArO*Me*), 62.91, 63.01 [$PO(OCH_2Me)_2$], 69.03 ($CHMe_2$), 74.79 (d, $J_{C,P}$ 152.13), 113.62, 115.61, 151.00, 151.50 (aromatics) and 165.90 (*C*=O); *m/z* (EI$^+$) 255 (10), 241 (22), 137 (18), 124 (20), 106 (22), 96 (21), 84 (20), 72 (21), 58 (70) and 45 (100).

General Procedures for the Reactions to Probe the Effect of the Catalyst.
The rhodium catalyst (1 mol%) was added to a mixture of 2-propanol (1 mole equiv.) and the relevant diazo compound (1 mole equiv.) in either toluene or dichloromethane (25 ml) (depending on the temperature at which the reaction was to be undertaken). The reaction was carefully monitored by TLC and when all the diazo compound had been consumed the solvent was removed *in vacuo* and analysed by ^{1}H NMR. The products were identified by comparison of this spectrum with that of the authentic materials.

Dimethyl 2-isopropyloxymalonate .
(58%), (Found: *M*+NH_4^+, 208.1185. $C_8H_{14}O_5$+NH_4 requires 208.1185); $\nu_{max.}$ (film)/cm^{-1} 2976, 1744, 1436, 1384, 1332, 1288, 1234, 1168, 1114 and 1024; δ_H 1.23 (6 H, d, *J* 6.2, Me_2CH), 3.80 (6 H, s, O*Me*), 3.80 (1 H, m, Me_2CH) and 4.59 (1 H, s, OCH); δ_C 21.87 ($OCHMe_2$), 52.83 (CO_2Me), 73.44 ($OCHMe_2$), 76.93 (COCH) and 167.63 (C=O); *m/z* (EI$^+$) 89 (14), 59 (19), 43 (100) and 39 (9).

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32. The isopropyloxy malonate has been prepared from the corresponding diazo compound by a method analogous to that of the diethyl analogue **23**. The details of this compound are described in the experimental section of this paper.
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