

Oxidation of Alkynes and Ylides by Oxo(salen)chromium(v) (salen = *N,N'*-ethylenebis-salicylideneiminato) Trifluoromethanesulphonate

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Oxo(salen)chromium(v) trifluoromethanesulphonate reacts with alkynes to afford diones, and with phosphorus ylides to afford aldehydes and ketones *via* similar organometallic intermediates.

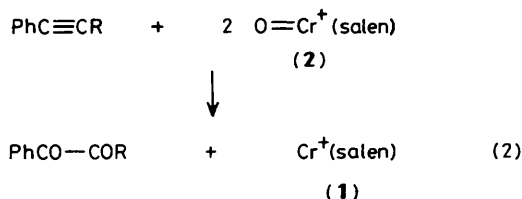
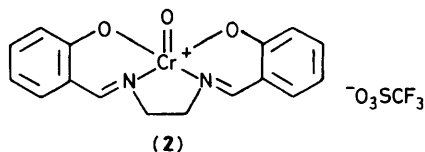
Chromium(III)-salen (salen = *N,N'*-ethylenebis-salicylideneiminato) derivatives (**1**) are active catalysts for oxygen atom transfer reactions.^{1,2} Oxygen atom donors such as iodosylbenzene oxidise (**1**) to the oxo(salen)chromium(v) complex (**2**). The chromium(III) and oxochromium(v) species have

been isolated and characterised by *X*-ray diffraction.¹⁻³ The oxochromium complexes oxidise alkenes to oxiranes as indicated in equation (1). The mechanism for the oxygen transfer has been proposed to involve the formation of organometallic intermediates.^{2,4} Understanding of the

Table 1. Reactions of (2) with carbene equivalents.

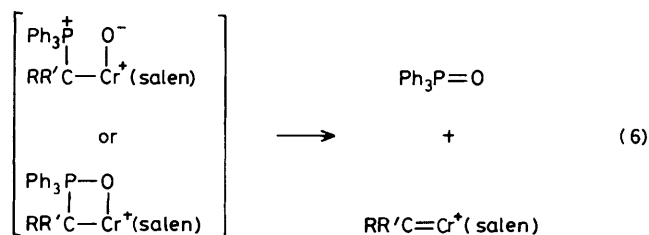
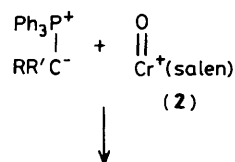
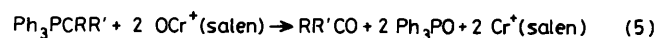
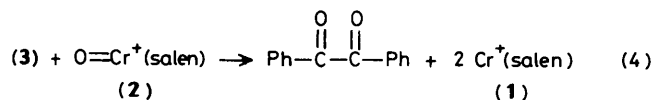
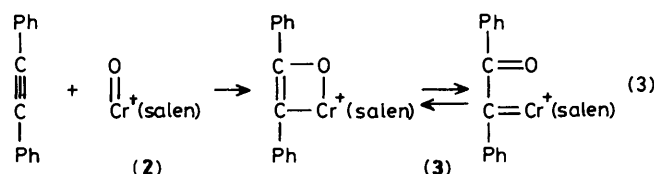
Substrate	Product	Yield ^a /%	Time ^b /min
PhC≡CPh ^c	PhCOCOPh	86	1400
PhC≡CH ^c	PhCOCHO	8	1400
	PHCO ₂ H	53	
Ph ₃ P=CHCO ₂ Et ^d	<i>E,Z</i> -EtO ₂ CCH=CHCO ₂ Et	48 ± 5(93) ^e	<5(60) ^e
Ph ₃ P=CMeCO ₂ Et ^d	MeCOCO ₂ Et	78	<5
Ph ₃ P=CHCOPh ^d	<i>E</i> -PhCOCH=CHCOPh	10 ± 1 (7 ± 2) ^e	45 (1000) ^e
	PhCOCHO	15 (2 ± 1) ^e	
	PhCO ₂ H	20 (95 ± 9) ^e	
Ph ₃ P=CHCH ₂ CH ₂ Me ^d	<i>E</i> -Pr ⁿ CH=CHPr ⁿ	43	30
	Pr ⁿ CHO	0 ± 1	
Ph ₃ P=CHPh ^d	<i>E,Z</i> -PhCH=CHPh	42	30
	PhCHO	23	

^a Based on (2) (0.1 mM in THF), determined by g.c.m.s. by comparison with authentic compounds. ^b For no further increase in product yields. ^c Alkyne present in twenty-fold excess. ^d Stoichiometric amount of ylide added in one portion to (2) in THF at room temperature under argon. ^e Ylide added in ten 0.1 equiv. increments.



mechanism of these reactions is important in the development of selective oxidation catalysts as well as in interpreting the role of metals at the active sites of biological catalysts. The ability to quantify the metal species (1) and (2) facilitates investigation of their oxidations. In order to examine the possibility of metal-carbon bonding between oxidant and substrates, we have studied the reactions of these metal complexes with alkynes. Oxirenes are unstable species⁵ and their formation [by analogy to equation (1)] should be disfavoured. Therefore, reactions of alkynes will differ from those of alkenes, and organometallic intermediates formed from an alkyne and the oxometal might be longer-lived.

Diphenylacetylene (2 mM) was found to react slowly with (2) (0.1 mM) in 10 ml of tetrahydrofuran (THF) under argon to afford benzil in 86% yield [equation (2), R = Ph]. The reaction of phenylacetylene (R = H) was not as clean, giving not only the dione but also benzoic acid in significant amounts (Table 1). Control experiments demonstrated that benzoic acid is formed by subsequent oxidation of phenylglyoxal. The delivery of *two* oxygens indicates that these reactions must occur in a stepwise fashion, and a second equivalent of oxochromium complex apparently traps an intermediate



formed by reaction of the alkynes with oxochromium complex. Formation of a metallocyclic and/or alkylidene intermediate (3) [equation (3)], which can be oxidized by (2) to form a dione in a second step [equation (4)], most simply explains these results.

The oxochromium cation has been shown to behave as an electrophilic oxidant.² The reaction of (2) with nucleophilic carbene equivalents is expected to produce intermediates closely related to (3). Therefore, the reactions of phosphorus ylides with (2) were examined. The charge distribution in ylides concentrates electron density on the ylide carbon, $Ph_3P=CRR' \leftrightarrow Ph_3P^+-CRR'$, which participates in reactions

(such as the Wittig reaction) distinctly as a nucleophile.⁶ Therefore, the ylide carbon would be expected to develop a strong interaction with the oxometal complex which should promote carbon-metal bonding.

Addition of one equivalent (0.1 mM) of a phosphorous ylide to a solution (10 ml in THF) of (2) under argon resulted in rapid consumption of both reagents and the formation of organic products (Table 1). Ylides which contained a mono-substituted ylide carbon afforded aldehydes and symmetrically substituted alkenes as major volatile products. The mass balance was high when the concentration of ylide was low. Disubstituted ylides afforded ketones (equation 5). As was found for reaction of alkenes² (equation 1), reaction of ylides was catalytic with respect to chromium in the presence of excess iodobenzene as terminal oxidant, with a turnover number of *ca.* 5.

Electrostatic considerations suggest that addition of an ylide to an oxometal cation may occur in the fashion indicated in equation (6). An analogous addition of phosphorus ylides to an oxomolybdenum(VI) species has been described.⁷ A variety of metal methylene complexes have been prepared by reaction of metal compounds with carbene precursors.^{8,9} Related metal methylene complexes have been shown to be quite reactive.⁸ Attempts to characterize intermediate species and assess the effects which might arise from specific interactions with the metal are in progress. The observed products may arise following the formation of alkylidene intermediates, as shown in equation (6), by reaction of the alkylidenes with a second equivalent of (2) (see equation 4). Formation of a carbonyl compound, followed by a Wittig reaction, would produce an alkene. Control experiments established that reactions between the aldehydes and ylide are fast and afford similar proportions of stereoisomers. Reactions between ketones and the disubstituted ylides were too slow to produce alkene under the reaction conditions.

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