

## Tungsten Wittig Reagents: an Efficient Synthesis of $\alpha$ -Functionalised Tri- and Tetra-substituted Alkenes

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


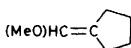
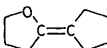
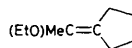
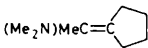
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The reaction of tungsten alkylidene complexes of the type  $W(=CR^1R^2)X_2Y_2$  with organic carbonyl groups is shown to enable a variety of di-, tri-, and tetra-substituted alkenes to be synthesised directly, including enol ethers and enamines.

The Wittig reaction by which an organic carbonyl function is transformed into an alkene by means of a phosphorus ylide is not generally applicable to less reactive carbonyl groups as in esters, lactones, or amides.<sup>1</sup> Partly, this restriction has been


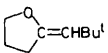
overcome recently by the use of alkylidene complexes of Ta,<sup>2</sup> Ti,<sup>3</sup> Zr,<sup>4</sup> and Mo,<sup>5</sup> but such reagents are limited to only certain alkylidene groups, *e.g.* sterically bulky (such as neopentylidene) or methylidene. We have recently reported that a

**Table 1.** Wittig-type reactions using  $W[=C(CH_2)_3CH_2](OCH_2Bu^t)_2X_2$  ( $X = OCH_2Bu^t$ , Cl, Br, or I).<sup>a</sup>

Substrate	$PhHC=O$	$Me_2C=O$	$(MeO)HC=O$		$(EtO)MeC=O$	$(Me_2N)MeC=O$
Product						
Ligands						
$(OCH_2Bu^t)_4$	25 °C, <0.1 h 88%	25 °C, 0.17 h 82%	25 °C, 3 h 82%	25 °C, 24 h 85%	25 °C, 40 h 76%	50 °C, 48 h 72%
$(OCH_2Bu^t)_2Cl_2$		25 °C, 1 h 90%		25 °C, 36 h 85%		
$(OCH_2Bu^t)_2Br_2$		25 °C, 2.5 h 95%		25 °C, 72 h <sup>b,c</sup> 75%	— <sup>c</sup>	
$(OCH_2Bu^t)_2I_2$	25 °C, 4.5 h 95%	25 °C, 30 h 95%		— <sup>c</sup>	— <sup>c</sup>	

<sup>a</sup> All reactions were carried out in deuteriobenzene with a stoichiometric amount of substrate. Inorganic compounds were not analysed. Organic products were distilled and analysed qualitatively and quantitatively by <sup>1</sup>H n.m.r. spectroscopy and g.c. Yields were measured before distillation and are based on tungsten complexes. <sup>b</sup> In  $CD_2Cl_2$ . <sup>c</sup> No reaction occurs at 25 °C in benzene; at 70 °C a different and not yet identified compound is obtained as major product.

**Table 2.** Wittig-type reactions using  $W(=CHBu^t)(OCH_2Bu^t)_2X_2$  ( $X = OCH_2Bu^t$ , Br, or I).<sup>a</sup>

Substrate	$PhHC=O$	$Me_2C=O$		$(EtO)MeC=O$
Product	$PhHC=CHBu^t$ <sup>b</sup>	$Me_2C=CHBu^t$		$(EtO)MeC=CHBu^t$
Ligands				
$(OCH_2Bu^t)_4$	25 °C, <0.1 h 95% <i>trans/cis</i> = 80/20	25 °C, 2.5 h 92%	25 °C, 48 h 85%	25 °C, 72 h 80%
$(OCH_2Bu^t)_2Br_2$	25 °C, 0.1 h 90% <i>trans/cis</i> = 70/30			
$(OCH_2Bu^t)_2I_2$	25 °C, 24 h 90% <i>trans/cis</i> = 65/35	25 °C, 72 h 88%	— <sup>c</sup>	

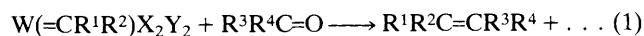
<sup>a,c</sup> See footnotes a and c in Table 1. <sup>b</sup> Assignment of *cis*- and *trans*-isomers was done previously.<sup>2</sup> The *E*- and *Z*-isomers of  $CH_2(CH_2)_2OC=CHBu^t$  and  $(EtO)MeC=CHBu^t$  were not distinguished.

**Table 3.** Wittig-type reactions using  $W(=CHR)(OCH_2Bu^t)_2I_2$  ( $R = Ph$  or  $Bu^n$ ).<sup>a</sup>

Substrate	$PhHC=O$	$Me_2C=O$
Ligands		
$(=CHPh)$	$PhHC=CHPh$ 25 °C, 2.5 h 94% <i>trans/cis</i> = 98/2	$Me_2C=CHPh$ 25 °C, 10 h 91%
$(=CHBu^n)$	$PhHC=CHBu^n$ 25 °C, <0.08 h 77% <i>trans/cis</i> = 60/40	$Me_2C=CHBu^n$ 25 °C, 4 h 70%

<sup>a</sup> cf. Table 1.

family of tungsten alkylidenes of the type  $W(=CR^1R^2)X_2Y_2$  ( $R^1, R^2 = \text{alkyl, aryl etc.}$ ,  $X, Y = \text{anionic ligands, halides, alkoxides, toluene-}p\text{-sulphonates etc.}$ ) can be conveniently synthesised from the corresponding alkene  $R^1R^2C=CH_2$ .<sup>6</sup> We now find that certain of such compounds react very readily with a wide variety of carbonyl functions to produce in high yield di-, tri-, and tetra-substituted alkenes including enol ethers and enamines [reaction (1)]. Moreover we show that the reactivity of such tungsten complexes can be controlled conveniently by changing the ligands  $X$  and/or  $Y$ .



Our results are summarised in Tables 1–3. We observe (i) the tetra-alkoxylated complexes  $W(=CR^1R^2)(OCH_2Bu^t)_4$  are powerful Wittig reagents, reacting with esters or lactones at room temperature, and amides at 50 °C. Good yields in alkene are obtained in all cases, the reaction rates decreasing as expected in the order aldehydes > ketones > formates > esters > amides.

(ii) Replacement in the alkylidene tungsten complexes of two neopentoxo groups by less  $\pi$ -donating chloro, bromo, or

iodo ligands induces a progressive and significant drop in reactivity. This probably results from a decrease in negative charge on the alkylidene carbon, previously suggested by n.m.r.<sup>6</sup> Aldehydes and ketones are, however, converted in high yields in all cases.

(iii) The rate of the reaction is also strongly dependent on the alkylidene group, decreasing in the order *n*-pentylidene > benzylidene > cyclopentylidene > neopentylidene, no doubt resulting from the increasing steric crowding about the alkylidene function.

(iv) A high *trans* stereoselectivity is observed with benzaldehyde as substrate, particularly in the case of the benzylidene group (Table 3), and increases moreover with the electron donating character of the ligands (Table 2). Interestingly, this is similar to the results obtained with phosphorus ylides  $R_3P=CHR'$ .<sup>7</sup> The reverse selectivity however has been reported for  $(Bu^tCH_2)_3Ta(CHBu^t)_2$  and  $(\eta^5-C_5H_5)_2(PPh_3)Zr(CHCH_2Bu^t)$ .<sup>8</sup>

In view of the significant differences in reactivity patterns between these tungsten reagents and their phosphorus counterparts, we have begun to investigate the mechanism of these reactions. We find that a rapid co-ordination of the carbonyl function initially occurs to the electron deficient tungsten centre. For example, n.m.r. studies show that the co-ordination of  $Me_2CO$  to  $W(CHBu^t)(OCH_2Bu^t)_2I_2$  occurs in  $C_6D_6$  to form the mono-adduct with a formation constant at 25 °C of  $1.75 \text{ dm}^3 \text{ mol}^{-1}$ . We note with other donor ligands such as pyridine that this prior co-ordination occurs *trans* to the alkylidene ligand, but is followed by a slow subsequent isomerisation process to form a *cis* adduct.<sup>9</sup> We would expect of course the need for such a *cis* relationship between the alkylidene ligand and co-ordinated carbonyl group if the alkylidene transfer were intramolecular. However we note that the most active complexes,  $W(=CR^1R^2)(OR)_4$ , show the weakest Lewis acidity, which would indicate that such co-ordination/isomerisation processes if involved in such reactions are no doubt not rate determining.

Finally, the control of the type of reactivity followed by these tungsten alkylidenes (e.g. Wittig or alkene metathesis<sup>6,10</sup>) by varying the nature of the other ligands  $X, Y$  on the metal can also be exploited in stereo- and regio-control in such and similar reactions.

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