Regiospecific Insertion of Benzylidene Ligands into the α-C–H Bond of Ethers

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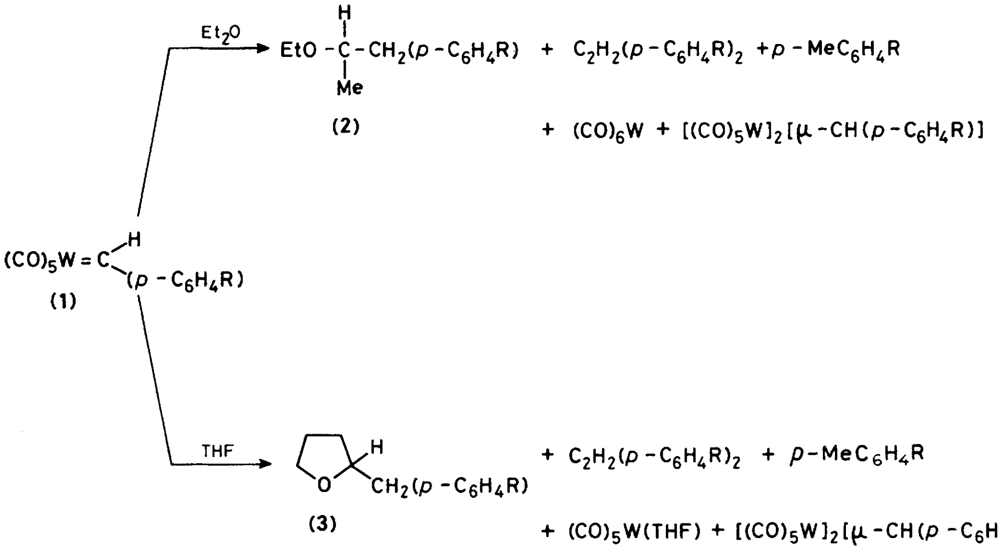
The benzylidene complexes $(CO)_5W{=}CH(p\text{-}C_6H_4R)$ (R = H, Me) react with diethyl ether or tetrahydrofuran to give regiospecifically the products of the insertion of the benzylidene ligand into the α-C–H bond of the ethers; the insertion reaction follows an associative mechanism initiated by a nucleophilic attack of the ethers at the benzylidene ligand.

Metal-bound carbene groups are believed to play a pivotal role in several catalytic processes. One of the elementary reaction steps in some of these processes may involve insertion of the co-ordinated carbene into a carbon–hydrogen bond. However, whereas the insertion of the co-ordinated carbene in $L_nM{=}CR^1R^2$ into an X–H bond (X = Si,[1,2] Ge,[2] Sn,[2] P,[3] O,[4] Se,[5] or Br[6]) is well documented, the insertion into a carbon–hydrogen bond (a characteristic feature of free carbenes) has not been observed until now. We now report the first insertion of a benzylidene ligand into a C–H bond. The insertion occurs regiospecifically into the α-C–H bond of ethers and in very high yield.

When dark red solutions of the benzylidene(pentacarbonyl)-tungsten complexes $(CO)_5W{=}CH(p\text{-}C_6H_4R)$[7] (**1**) in diethyl



a; R = H
b; R = Me

Scheme 1

ether are allowed to warm from −78 °C to room temperature, the solution turns brown and $EtOCH(Me)CH_2(p\text{-}C_6H_4R)$ (**2**) is formed in high yield (>90%) (Scheme 1). At ambient temperature the reaction is complete within *ca.* 2—3 min. The compounds (**2**) which correspond to the product of the insertion of the benzylidene ligand into the α-C–H bond of diethyl ether were identified by g.c., ^1H n.m.r., and mass spectroscopy and, in the case of (**2a**), additionally by comparison with an authentic sample.[8] Besides (**2**), small amounts of the *cis-* and *trans-* stilbenes and $p\text{-}MeC_6H_4R$ as well as $(CO)_6W$ and small amounts of the μ-benzylidene complexes $[(CO)_5W]_2[\mu\text{-}CH(p\text{-}C_6H_4R)]$[7] were obtained. Neither the β-C–H insertion product nor benzyl ethyl ether (which constitutes one of the major products when phenyldiazomethane is photolysed in diethyl ether at 0 °C [9]) and *p*-methylbenzyl ethyl ether, respectively, could be observed. The formation of more than 0.2% of each compound would have been detected.

The analogous reaction of (**1**) with tetrahydrofuran (THF) yields α-benzyltetrahydrofuran and α-(*p*-methylbenzyl-tetrahydrofuran (>90%), respectively. The $(CO)_5W$-fragment is stabilized by THF giving $(CO)_5W(THF)$ (Scheme 1). Again, the β-C–H insertion product could not be detected.

The kinetics of the reaction of (**1b**) with THF in THF–octane at 15.1 °C were studied by following the disappearance of the $\nu(CO)\text{-}A_1{}^2$-absorption of (**1b**) at 2072 cm^{-1} in the i.r. spectrum. Pseudo-first order conditions $\{[(\mathbf{1b})]_0:[THF]_0$ ranging from 1 : 307 to 1 : 1500$\}$ were employed. The rate constants were reproducible to at least 7%. The reaction follows an additive rate law: $-d[(\mathbf{1b})]/dt = k_1[(\mathbf{1b})] + k_2[(\mathbf{1b})][THF]^2$. At 15.1 °C, $k_1 = 1.6 \times 10^{-4}\ s^{-1}$ and $k_2 = 4.6 \times 10^{-4}\ dm^6\ mol^{-2}\ s^{-1}$ {from a plot of k_{obs} *vs.* $[THF]^2$; seven pairs of k_{obs} and $[THF]^2$, correlation coefficient better than 0.996}. When THF was replaced by $[^2H_8]$THF, an isotope effect of $k_2{}^H/k_2{}^D = 1.7$ was observed.

The first-order term coincides with the independently determined rate of thermolysis of (**1b**) in octane ($k_{obs} = 1.64 \times 10^{-4}\ s^{-1}$, at 15.1 °C) giving rise to the formation of the *cis-* and *trans*-stilbenes, $p\text{-}C_6H_4Me_2$, and $[(CO)_5W]_2[\mu\text{-}CH(p\text{-}C_6H_4Me)]$ which are the characteristic thermolysis products of (**1b**) in inert solvents.[7] α-(*p*-Methylbenzyl)tetrahydrofuran is produced by an associative mechanism (third-order term) thus accounting for the regiospecificity of the insertion. This reaction is initiated by a nucleophilic attack of THF at the strongly electrophilic benzylidene carbon of (**1b**). The yield of (**3b**) drops drastically with decreasing concentration of THF, in agreement with the second-order THF term in the rate expression.

When similar conditions are employed, (**1a**) reacts with THF *ca.* three times faster than (**1b**). Et_2O–THF competition experiments show that the insertion of '$CH(p\text{-}C_6H_4Me)$' into the α-C–H bond of THF is favoured by a factor of ten.

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