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Preliminary communication

NOVEL MECHANISM FOR THE CARBONYLATION AND HYDROFORMYLATION OF OLEFINS VIA CARBENE AND KETENE TYPE INTERMEDIATES

LAJOS BENCZE and LÁSZLÓ PRÓKAI

Veszprém University of Chemical Engineering, Institute of Hydrocarbon and Coal Processing, P.O.B. 158, H-8201 Veszprém, (Hungary)

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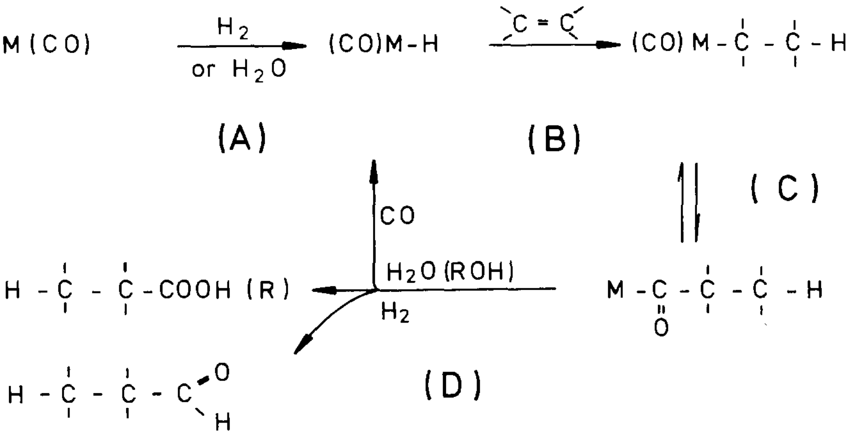
Summary

Stoichiometric hydroformylation and carbonylation of norbornene takes place in the presence of $W(CO)_3Cl_2(AsPh_3)_2$ and water or alcohol via initial formation of carbene and ketene type intermediates followed by nucleophilic addition of water or alcohol or a hydrido-metal species to the carbon—oxygen double bond of the ketene.

The carbonylation and hydroformylation of olefins are the most used and studied transition metal catalyzed reactions of carbon monoxide. Although these processes can involve various metals and ligands, and a wide range of reaction conditions, it is generally accepted that the reactions can be described qualitatively in terms of four main reaction steps [1] (Scheme 1).



SCHEME 1

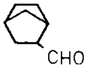
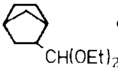
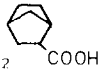
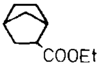
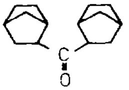
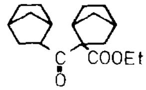
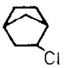
The first step is the formation of a transition metal hydride (A) followed by olefin insertion into the metal—hydrogen bond (B). Then a coordinated carbon monoxide molecule inserts into the carbon—metal σ bond (C), and the cycle is completed by a nucleophilic attack on the acyl—metal intermediate (D). The product is an acid, an ester or an aldehyde, depending on the nucleophile used.

We recently reported that when $W(CO)_3Cl_2(AsPh_3)_2$ reacts with norbornene under mild conditions a tungsta-2-norbornylidene species is formed by a 2,3-hydrogen shift in the coordinated alkene [2]. This complex carbene initiates the ring-opening polymerisation of the excess of norbornene [3] or reacts with the carbon monoxide ligands to form carbonylene norbornane.

In a typical experiment a solution of 10 mmol of norbornene and 0.1 mmol of $W(CO)_3Cl_2(AsPh_3)_2$ in 50 ml of benzene was kept at 80°C under dry argon for 1 h. Ethanol was then added and the products were analysed by GC-MS. The predominant low molecular-weight product was ethyl-2-norbornane-carboxylate ester (Table 1, run 1).

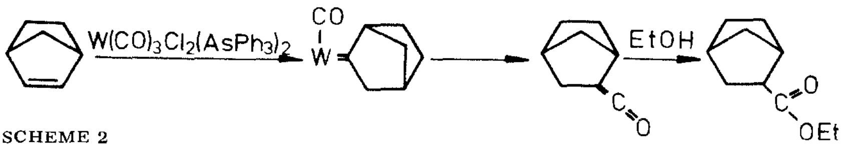
Table 1

Products from $W(CO)_3Cl_2(AsPh_3)_2$ + norbonene + H_2O and / or EtOH

Run	Products, %						
							
1	2	2	-	88	1	1	6
2	23	0	a	0	8	-	69
3[b]	3	13	a	35	7	-	42

[a] Not quantitatively determined.
[b] Deuterated products, see text.

Besides the novelty of the direct synthesis of a ketene the main feature of this reaction is that a conventional carbonylation product, an ester, is formed from CO, olefin and alcohol in a way which does not involve any of the steps A—D of the conventional carbonylation mechanism, i.e. none of the hydrido-, alkyl-, or acyl-metal intermediates is needed to describe this oxo reaction (Scheme 2).



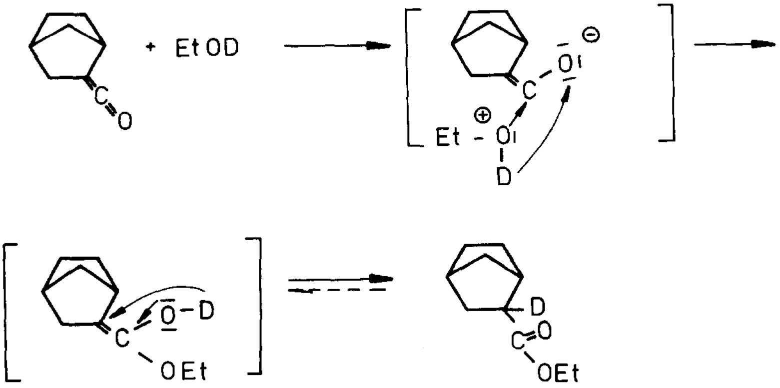
SCHEME 2

Detailed GC-MS studies of the products revealed that in the presence of moisture 2-formyl-norbornane is formed, along with some hydrolysis and alcoholysis products of the diketene, such as di-(2- norbornyl)-ketone and its 2-carboxyethyl derivative. Some 50% of the aldehyde was found in the diethylacetal form.

The total yield of the carbonylated and hydroformylated derivatives is comparable to the molar quantity of the transition metal complex used. Their relative quantities are given in Table 1. When water is used instead of alcohol for quenching the reaction an increased amount of aldehyde and ketone was found in the organic layer, and some 2-norbornane-carboxylic acid was detected in the aqueous phase (run 2).

When the reaction was carried out in the presence of D_2O (6 mmol) and quenched with EtOD the relative quantity of hydroformylated products was also enhanced (Table 1, run 3) as was that of di-(2-norbornyl)-ketone-2,2'-d_2. Each of the compounds contained exclusively one D atom for each norbornane unit in position 2 of the norborane skeleton, except for the formyl derivatives, which contained an additional deuterium atom at the carbonyl carbon. The position of the deuterium atoms suggests that carbonylene-2-norbornane, i.e. a ketene, is a common intermediate in formation of the carbonylated and the hydroformylated products, and that the transient carbene is formed by an intramolecular 2,3-hydrogen shift in the coordinated norbornene.

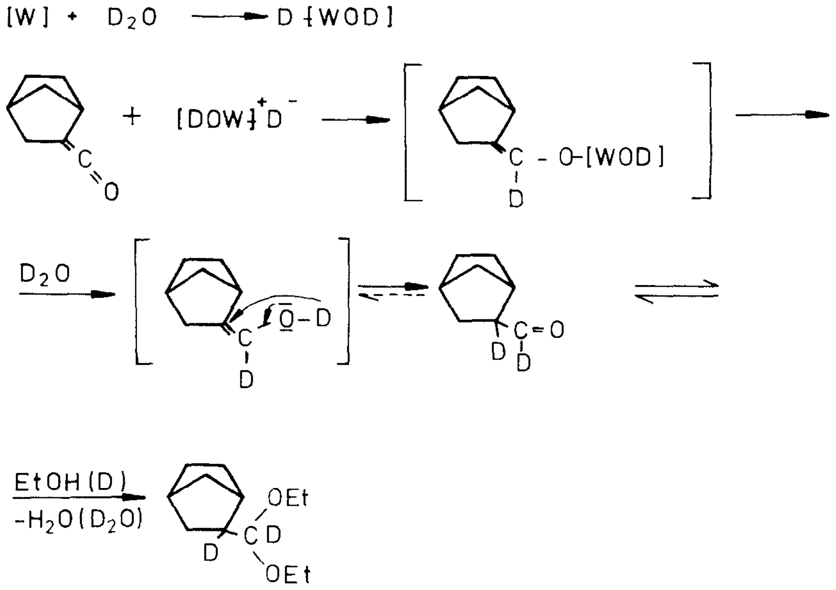
The source of hydrogen or deuterium for the reduction is undoubtedly the water. It can be readily envisaged that both the ester and aldehyde formation begin with a nucleophilic addition to the CO double bond of the ketene. In the first case the nucleophile is the alcohol, and the ester is formed by the tautomeric rearrangement of the transient ketene-hemiketal, as in Scheme 3.



SCHEME 3

In the formation of the aldehyde a complex tungsten hydride, derived from the oxidative addition of water to the metal complex is assumed to be the nucleophile, as in Scheme 4.

The metal hydride adds to the CO double bond of the ketene forming an enolate in the way that many organometallic compounds do [4—6]. Subsequent hydrolysis of the enolate and the tautomeric rearrangement of the enol is in accordance with the experimental results.



SCHEME 4

Formation of ketones is one of the most characteristic side reactions in oxo synthesis. It is generally accounted for in terms of repeated insertion of the same carbonyl group into two σ C—M bond. The deuterated products obtained in our experiments indicate that the ketone or the ketoester are simply the hydrolysis or alcoholysis products of the corresponding diketene.

Experiments using $W(CO)_4Cl_2$ as catalyst gave essentially the same results.

Preliminary results on the carbonylation of 2-pentene indicate that this novel mechanism may be of more general validity.

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