Mechanism of Initiation of the Metathesis of Norbornene using $W(CO)_3Cl_2(AsPh_3)_2$ as Catalyst

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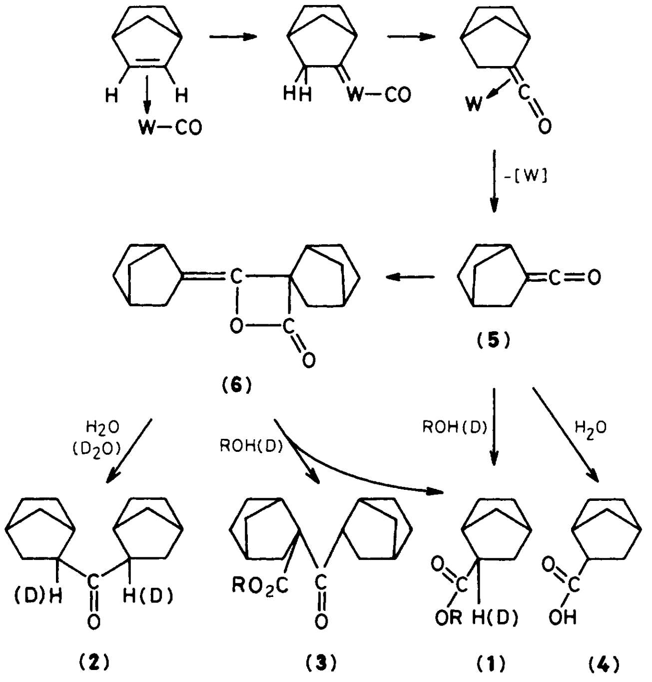
Low molecular-weight derivatives obtained during ring-opening polymerisation of norbornene using $W(CO)_3Cl_2(AsPh_3)_2$ as catalyst indicate that a 2,3-hydrogen shift is a key step for the formation of the carbene initiator.

Catalyst systems having neither a preformed metallacarbene nor an alkyl group in any component represent a relatively minor class of metathesis initiators. While some recent investigations[1,2] point to a hydrogen transfer process in W-complexes with alkenes, pathways for carbene formation are in most cases unresolved.

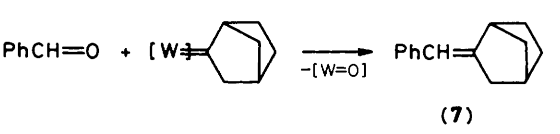


Scheme 1. R = Me or Et.

We reported recently that the ring-opening polymerization of norbornene (10 mmol) occurs readily in benzene solution (50 ml) at 80 °C using $W(CO)_3Cl_2(AsPh_3)_2$ (0.05 mmol) as catalyst.[3] In order to elucidate the mechanism of carbene initiation the reaction was quenched by EtOH and the low molecular-weight products were identified by g.c.–mass spectrometry and comparison with authentic samples. The major product was ethyl norbornane-2-carboxylate (**1**) (*m/z* 168(2.8%; M^+), 139(11), 123(13), 101(100), 95(86), 73(24), 67(30), 66(14), and 41(12). Smaller amounts of di-(2-norbornyl)ketone (**2**) (M^+, *m/z* 218, 5%) and the 2-ethoxycarbonyl derivative (**3**) (M^+, *m/z* 290, 0.7%) were also found besides some 2-chloronorbornane. Using methanol as a quenching agent the corresponding methyl derivatives of (**1**) and (**3**) were identified.

When water was added to the system ($H_2O/W = 11$) prior to the polymerization and the reaction quenched with a large quantity of cold water the polymer yield dropped from 65 to 10%. An increased quantity of (**2**) and 2-chloronorbornane was found in the benzene solution while the esters were missing. The acid (**4**) (M^+, *m/z* 140, 11.3%) was identified in the aqueous phase.

The mechanisms of formation of (**1**)—(**3**) and (**4**) are



Scheme 2

intimately connected: they appear to be products of addition of water or alcohols to the ketene (**5**) and its dimer (**6**) by analogy with the reactions of ketoketenes reported by Anet[4] and Hasek *et al.*[5]

This idea is further strengthened by the observation that when the system is partially poisoned by addition of D_2O prior to the polymerization and then quenched by EtOD the ester (**1**) formed is exclusively monodeuteriated, and the deuterium is situated in position 2. The ketone (**2**) contains two D atoms, each on the α carbon atoms, *i.e.* in position 2 of the norbornane skeleton. These results show that the corresponding C-8 ketene is formed without any H–D scrambling, which occurs only in the hydrolysis or alcoholysis step (Scheme 1).

The reversible generic relationship between carbenes and ketenes *via* CO–carbene coupling and decoupling is well known in organic chemistry[6,7] and has recently been recognized in organometallic chemistry[8—11] also. It is readily envisaged now that the structure of the initial carbene ligand may be identified with a co-ordinated 2-norbornylidene species, and the ketene is formed by coupling with a neighbouring carbonyl ligand.

It is therefore to be expected that the activity of the catalytic system will be rather sensitive to carbene-trapping reagents, such as organic carbonyl compounds.[12] Thus, when benzaldehyde was added to the norbornene–$W(CO)_3Cl_2(AsPh_3)_2$–benzene system prior to thermal activation, the ring-opening polymerisation was inhibited and the benzylidene-norbornane (**7**) (M^+, m/z 184, 27%) was formed as the major product of a Wittig-type carbene–aldehyde reaction (Scheme 2).

This further supports the assumption that the hydrocarbon part of the initiating metallacarbene complex may be identified with a 2-norbornylidene group formed by a 2,3-(1,2-) hydrogen shift in the co-ordinated alkene.

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