

SYNTHESIS BY METATHESIS

II *. KINETICS OF METATHESIS OF ω -ARYLOLEFINS

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Summary

Kinetic studies of metathesis of ω -arylolefins have been performed with two types of catalytic systems derived from molybdenum and tungsten. The effect of the structure of these olefins on their reactivity has been studied in terms of three variables: length of the chain between the aromatic ring and the double bond, substituent effects at the double bond, and substituent effects on the aromatic ring. The results are discussed in terms of a "one carbene" exchange mechanism, on the basis of steric and electronic effects of the olefin.

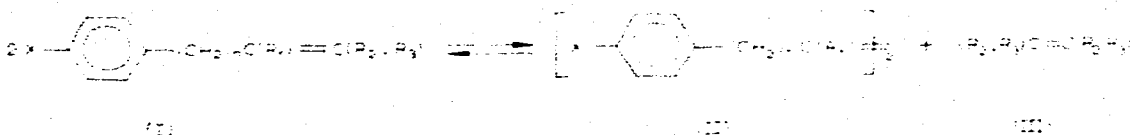
Introduction

Metathesis of acyclic and cyclic olefins has been the subject of much research in the past ten years [1-7]. The studies were mainly concerned with the reaction mechanism and the discovery of new catalytic systems. Although it seems fairly well established that the reaction proceeds by a "one carbene" exchange mechanism [8-12], and that the active catalyst is the same whatever the precursor complex used [13], little is known about the influence of steric effects of the starting olefin and its reactivity in metathesis. Dall'Asta [14] examined the ring opening polymerisation of 3-methyl-*cis*-cyclooctene and obtained information about the occurrence of head to head or head to tail successions. More than 90% of the polymer had a head to tail configuration, but the sterically more hindered and therefore unfavoured head to head links were also observed (about 5%).

* For part I, see ref. 18a.

Ofstead [15] investigated the ring opening polymerisation of some 1,5-cyclo-octadienes substituted at one of the two double bonds in the presence of WCl_6 , $C_2H_5AlCl_2$, C_2H_5OH . When one of the double bonds was substituted with an ethyl group, a chlorine atom, or two methyl groups, it virtually did not participate in the metathesis reaction, which indicates that steric factors are very important. However this does not seem always to be the case, since there are examples in which substituted olefins are cleaved by metathesis, especially with heterogeneous catalysts; for example, isobutene and propene can give a cross metathesis [16]. The results also may be complicated by thermodynamic restrictions; whereas it is usually assumed that metathesis is an equilibrium reaction giving about 50% conversion, this does not always apply to substituted olefins. For example, isobutene cannot give more than 1.4% of 2,3-dimethyl-2-butene at room temperature [7], and this could account for the fact that no significant metathesis has been observed for this compound at room temperature.

It was therefore of interest to make a systematic study of the influence of the structure of the olefin on its reactivity in metathesis. The olefins used were arylolefins I, which on metathesis give diarylolefins II and a volatile olefin III [18].



Three different parameters were investigated: (i) Influence of the chain length between the aromatic ring and the double bond on the kinetics of metathesis. (ii) Influence of methyl groups on the double bond on the kinetics of metathesis. (iii) Influence of electron donor or electron acceptor groups on the aromatic ring.

Kinetics studies were performed with two different catalytic systems: $Mo(NO)_2 \cdot Cl_2 [P(C_6H_5)_3]_2, C_2H_5AlCl_2$ [16]; $W(CO)_5P(C_6H_5)_3, C_2H_5AlCl_2, O_2$ [17].

Results

Influence of the chain length on the kinetics of metathesis

This study involved unsubstituted arylolefins I ($R_1 = R_2 = R_3 = H$). The chain length varied between $n = 0$ up to $n = 6$. In all the cases except $n = 0$, the reaction was possible and gave the expected ω, ω' -diarylolefin II along with ethylene. With styrene ($n = 0$) a fast polymerization occurred, and no metathesis products were formed. The initial rate of metathesis was determined for the molybdenum and tungsten complexes: a trend was observed with both catalytic systems, for a marked increase of the rate in the case of $n = 2$, that is for 4-phenyl-1-butene (Ib) (Table 1).

It must be noted for these α -olefins, that the molybdenum complex is more active than the tungsten one. We point out also that the initial rates were measured at very low conversion (<1%); if the reaction is carried on for a longer period, side reactions such as oligomerization [18] and double bond migrations of the starting olefin occur.

TABLE 1
METATHESIS OF ω -ARYLOLEFIN I ($R_1 = R_2 = R_3 = H$)

I $R_1 = R_2 = R_3 = X = H$	n	$Mo(NO)_2Cl_2[P(C_6H_5)_3]_2.C_2H_5AlCl_2$		$W(CO)_5P(C_6H_5)_3.C_2H_5AlCl_2.C$	
		$R_i \times 10^3^a$	% $C_2H_4^b$	$R_i \times 10^3^a$	% $C_2H_4^b$
a	1	6.2	8	1.4	1.5
b	2	20	16	7.5	2
c	3	12.5	13	1.1	0.6
d	4	11.5	13	0.9	0.7
e	6	4.4	10	0.9	0.6

^a Initial rate R_i : mol $C_2H_4 \times$ mol catalyst⁻¹ \times sec⁻¹. ^b % C_2H_4 at equilibrium.

Metathesis of substituted arylolefins

In this case, arylolefins were of the type I where R_1 , R_2 and R_3 could be H or CH_3 .

Table 2 shows clearly that metathesis does not occur with tetra- or tri-substituted double bonds or even disubstitution on the same ethylenic carbon atom. In the latter case, an intramolecular alkylation occurs [18], as in the case of 2-pentene metathesis in aromatic solvents [19,20].

In Fig. 1, are shown two kinetic curves for metathesis of allylbenzene (Ia) and *trans*-1-phenyl-2-butene (Ig) with the catalytic complex derived from molybdenum. It is noteworthy that a higher yield is obtained from the internal olefin than from the terminal one, although the initial rates are almost equal.

Figure 2 shows the variation with time of the *trans*-2-butene content. At low conversion, *trans*-1-phenyl-2-butene (Ig) gives preferentially *trans*-2-butene which indicates the same kind of stereoselectivity as that observed by Hughes et al. [17] for metathesis of 2-pentene. When conversion increases, the 2-butene composition slowly reaches the thermodynamic equilibrium as a result of *trans*-*cis* isomerization by a metathetic mechanism [22].

Substitutions on the aromatic ring for electron-donor or acceptor groups have been carried out with allylbenzene (Ia) as starting olefin. It can be seen that the presence of a *para*-methoxy group inhibits metathesis. Halogenes as well as methyl or *t*-butyl groups do not modify significantly the rate of metathesis compared to that observed with the starting olefin. Nevertheless the highest rates are observed when the substituent is H or F (Table 3).

TABLE 2
METATHESIS OF ω -ARYLOLEFINS I ($X = H$, $n = 1$)

I $X = H$ $n = 1$	R_1	R_2	R_3	$Mo(NO)_2Cl_2[P(C_6H_5)_3]_2.C_2H_5AlCl_2$		$W(CO)_5P(C_6H_5)_3.C_2H_5AlCl_2.O_2$	
				$R_i \times 10^3^a$	% III ^b	$R_i \times 10^3^a$	% III ^b
a	H	H	H	6.2	8	1.4	1.5
f	CH_3	H	H		alkylation [18]	0	0
g	H	CH_3	H	6.3	23	3	5
h	H	CH_3	CH_3		alkylation [18]	0	0
i	CH_3	CH_3	CH_3	0	0	0	0

^a Initial rate R_i : mol III \times mol catalyst⁻¹ \times sec⁻¹. ^b % III at equilibrium.

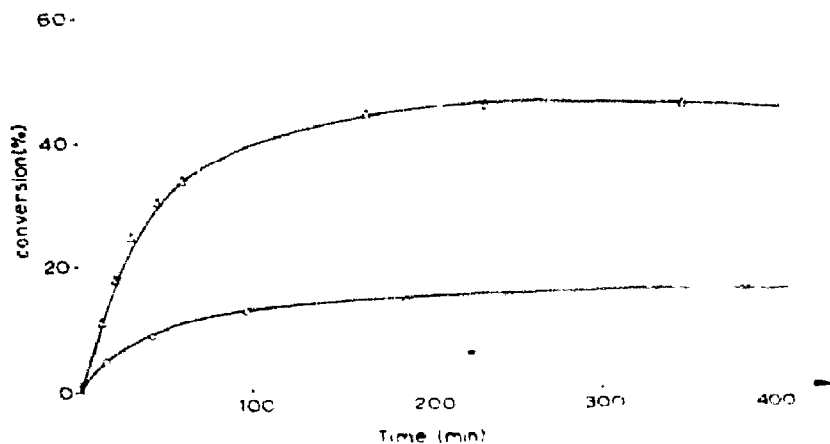


Fig. 1. Metathesis of allylbenzene (Ia) (●) and *trans*-1-phenyl-2-butene (Ig) (○).

Cross metathesis

Cross metathesis between cyclic and acyclic olefins is one of the best ways of obtaining an insight into the reaction mechanism. In this way, metathesis has been shown not to proceed by a pair-wise mechanism, but probably by a "one carbene" exchange [8,10,11].

We have performed the cross metathesis between two pairs of sterically different acyclic olefins, namely (i) 1-phenyl-2-butene (Ig) and 1-phenyl-3-methyl-2-butene (Ih) and (ii) allylbenzene (Ia) and 1-phenyl-2-butene (Ig). The results are shown in Table 4.

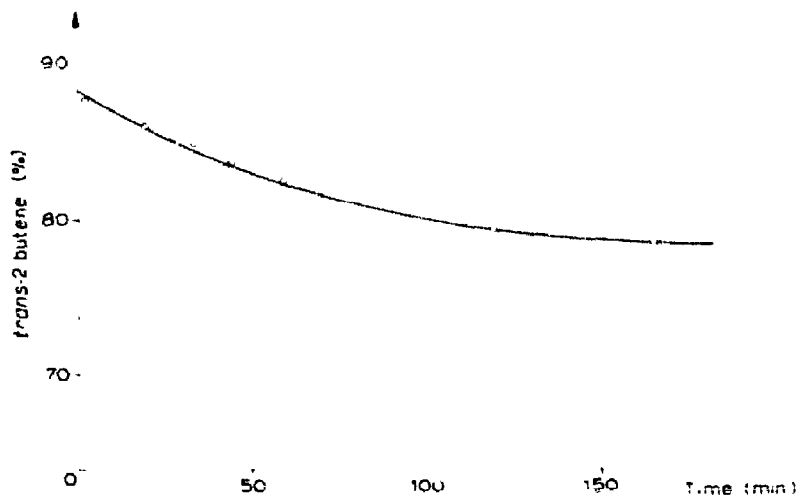


Fig. 2. Metathesis of 1-phenyl-2-butene (Ig), 90% *trans*. Percentage of *trans*-2-butene with time.

TABLE 3
METATHESIS OF ω -ARYLOLEFINS I ($R_1 = R_2 = R_3 = H, n = 1$)

I $R_1 = R_2 = R_3 = H$ $n = 1$	X	Mo(NO) ₂ Cl ₂ [P(C ₆ H ₅) ₃] ₂ . C ₂ H ₃ AlCl ₂		W(CO) ₅ P(C ₆ H ₅) ₃ C ₂ H ₅ AlCl ₂ O ₂	
		$R_1 \times 10^3$ ^a	% C ₂ H ₄ ^b	$R_1 \times 10^3$ ^a	% C ₂ H ₄ ^b
a	H	6.2	8	1.4	1
k	CH ₃	3.5	7.3	1.1	0.8
l	C(CH ₃) ₃	2.3	5.3	1	0.9
m	F	4.2	4.6	2.2	5.4
n	Cl	2.5	1.8	1.6	2.3
o	Br	3	6	1.2	1.2
p	OCH ₃	0	0	0	0

^a Initial rate R_1 : mol C₂H₄ × mol catalyst⁻¹ × sec⁻¹. ^b % C₂H₄ at equilibrium.

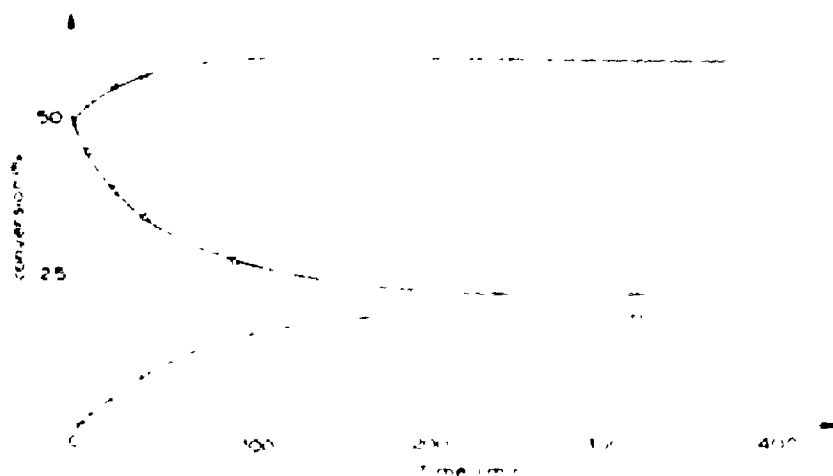


Fig. 3. Metathesis of *o*-allylbenzene (Ia) and *trans*-1-phenyl-2-butene (Ig). Percentages of 2-butene (—), ethylene (---), and propene (···) with time.

TABLE 4
CROSS METATHESIS: PERCENTAGES AT EQUILIBRIUM

I	% ethylene	% propene	% butene (Z + E)	% II
Ia + Ig	3	8	2.5	16
Ig + Ih	0	1.5	10	7

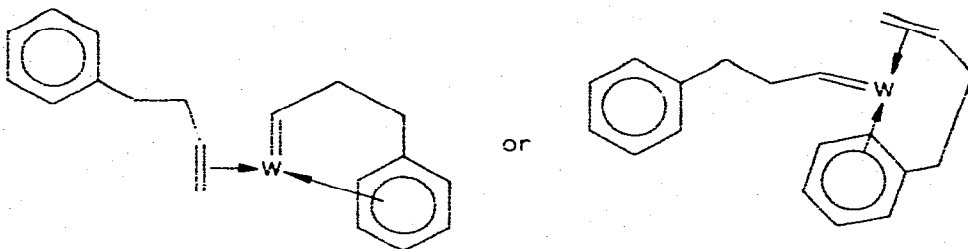
In the case of Ig + Ih, the only observed product is 2-butene. This indicates that the only reacting olefin is 1-phenyl-2-butene (Ig). Cross metathesis between a sterically hindered and a sterically non hindered olefin seems not to occur. The presence of 1-phenyl-3-methyl-2-butene (Ih) decreases the rate of metathesis of 1-phenyl-2-butene (Ig), but does not modify the final yield; this indicates that the bulky olefin is coordinated to the metal and does not react further.

Metathesis was also performed with an equimolecular mixture of allylbenzene (Ia) and 1-phenyl-2-butene (Ig). The product distribution at very low conversion was 50% ethylene and 50% propene with no 2-butene (Fig. 3). At equilibrium the mixture of 59% propene, 22% ethylene and 19% 2-butene was obtained. Obviously steric effects are responsible for this unexpected behaviour, since the product distribution at low conversion is totally different from the products expected from metathesis of both olefins taken separately (2-butene and ethylene).

Discussion

First we point out that, in agreement with Zuech [16,21], we found $\text{Mo}(\text{NO})_2\text{-Cl}_2\text{L}_2$ associated to $\text{C}_2\text{H}_5\text{AlCl}_2$ to be an efficient catalyst for metathesis of terminal as well as internal olefins. The catalytic system $\text{W}(\text{CO})_5\text{P}(\text{C}_6\text{H}_5)_3, \text{C}_2\text{H}_5\text{-AlCl}_2, \text{O}_2$ is a rather poor catalyst for α -olefins. Since it seems established that any precursor complex leads to the same active species [13], we could conclude that molybdenum complexes are more efficient for α -olefins, whereas tungsten complexes seem to be more suitable for internal olefins. This may be related to the relative stability and (or) reactivity of the metallocarbene moieties: ($\text{Mo}=\text{CH}_2$, $\text{W}=\text{CH}_2$, $\text{Mo}=\text{CHCH}_3$ and $\text{W}=\text{CHCH}_3$).

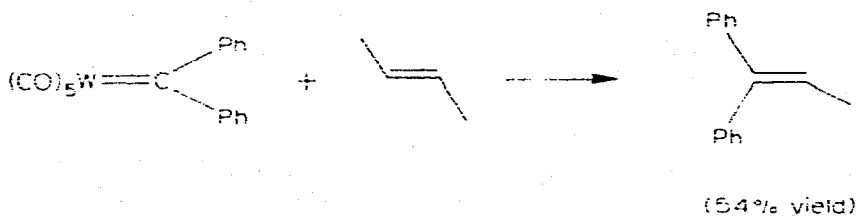
Our study of the influence of the chain length between the phenyl group and the double bond has shown a very high activity for the olefin Ib. Similar results have been obtained by Gleicher and Martin [23] in the case of the addition of the trichloromethyl radical to the same kind of aryl olefins. Our results can be rationalised on the same basis if we assume an interaction between the aromatic ring and the transition metal during one of the catalytic steps. The favoured coordination of the aromatic ring to the carbene can occur in two different ways shown in the following scheme:



This kind of interaction would decrease the mobility of, and therefore the steric hindrance by the aromatic group. Coordination of a second olefin and subsequent carbene exchange mechanism could thus be favoured. This would imply also that the coordination sphere of tungsten (or molybdenum) does not contain

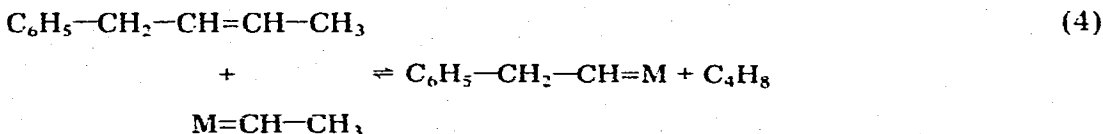
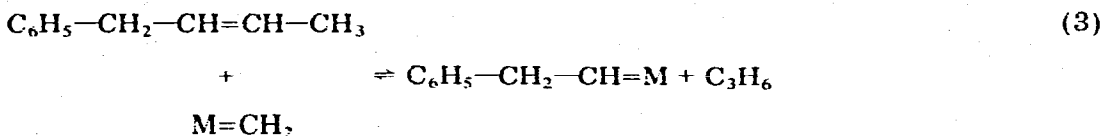
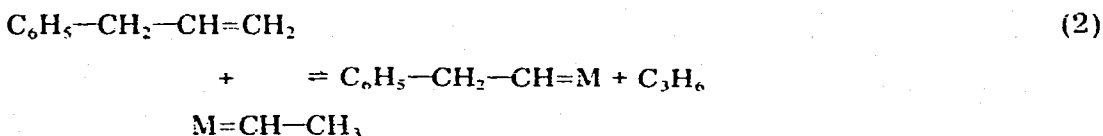
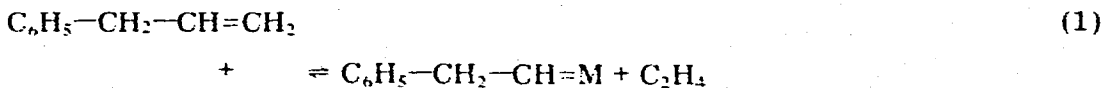
many ligands of the precursor complex, as we previously suggested on the basis of stereochemical studies [13].

Another aspect of our work deals with the steric and/or electronic effects at the double bond itself. A drastic effect is produced by the presence of more than one methyl group on the same carbon. This is difficult to rationalize except in terms of steric effects: recent results of Casey [11] seem to indicate that a bulky carbene ligand coordinated to tungsten is able to undergo a one carbene exchange mechanism with *trans*-2-butene by intramolecular process:



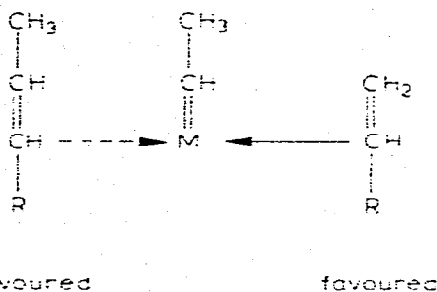
It is possible that in addition to these steric effects, the electrophilic nature of the carbene ligand may be very important.

The experiment on the cross metathesis between allylbenzene (Ia) and 2-phenyl-2-butene (If) seems to give a partial answer to the question of the importance of steric effects of the olefin. The absence of 2-butene at very low conversion can be rationalized as follows. Among all of the metallocarbene moieties present in the catalytic system, the only ones which can lead to the light olefins (ethylene, propene and 2-butene) are $M=CH_2$ and $M=CHCH_3$. Thus four different equilibria are possible:



The fact that at very low conversion no 2-butene is formed whereas ethylene and propene are formed in equal quantity indicates that reaction 4 does not proceed to the right although the carbene $M=CHCH_3$ is present. When the coordinated

carbene $M=CHCH_3$ is formed, any subsequent coordination of the olefin and (or) its exchange will depend on the steric environment of this olefin: the less hindered olefin, that is the terminal one, will be favoured:



Experimental

All the kinetic experiments were carried out with chlorobenzene as a solvent. It was distilled over P_2O_5 and kept under argon. $Mo(NO)_2Cl_2[P(C_6H_5)_3]_2$ and $W(CO)_5P(C_6H_5)_3$ were prepared as described by Cotton et al. [24] and Maggee et al. [25].

$C_2H_5AlCl_2$ was distilled under vacuum, dissolved in chlorobenzene and kept under argon. The starting olefins were distilled over Na or P_2O_5 and kept under argon. The olefins obtained by metathesis have already been characterized [18].

The equipment used for the kinetic studies has been described [17]. Reagents were introduced into the reactor in the following order: precursor complex, $C_2H_5AlCl_2$, propane (internal standard) and olefin. In the case of $Mo(NO)_2Cl_2[P(C_6H_5)_3]_2$, the catalyst and cocatalyst were allowed to react 30 min before introducing the olefin. The following ratios were used: $C_2H_5AlCl_2/Mo(NO)_2Cl_2[P(C_6H_5)_3]_2 = 7.5$; olefin/ $Mo(NO)_2Cl_2[P(C_6H_5)_3]_2 = 125$.

In the case of $W(CO)_5P(C_6H_5)_3$, molecular oxygen was introduced last and the following ratios were used: $C_2H_5AlCl_2/W(CO)_5P(C_6H_5)_3 = 4$; olefin/ $W(CO)_5P(C_6H_5)_3 = 100$; $O_2/C_2H_5AlCl_2 = 1.5$.

The initial rate of metathesis was determined by chromatographic analysis of the gaseous phase in the reactor, and thus only the rate of appearance of the light olefins was measured. Real concentrations in the liquid phase were obtained by preliminary standardisations.

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