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STEREOSPECIFIC POLYMERIZATIONS OF CYCLOALKENES INDUCED BY A METAL-CARBENE

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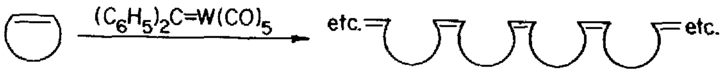
Since olefin metatheses are thought to be brought about by chain reactions propagated metal-carbenes,[1] it seemed worthwhile to see whether metal-carbenes[2] themselves initiate polymerizations of cycloalkenes.[3] Kroll and Doyle had found mixtures of some metal-carbenes, methylaluminum dichloride, and tetrabutylammonium salts effective,[4] and such combinations convert cyclooctene to a polyoctenamer that is largely trans and cyclopentene to a polypentenamer that is 90% trans.[5] We have found that (diphenylcarbene)pentacarbonyltungste alone, without added cocatalysts, is an effective initiator of metatheses of numerous cis-cycloalkenes,[7] converting them into polyalkenamers 90% or more of whose double bonds are cis (equation 1). Cyclobutene, cyclopentene, cycloheptene, cyclooctene, and norbornene a



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all transformed in this way. The resulting polymers are all soluble in toluene or benzene a their molecular weights are high.

Previously the only cis polyalkenamers to have been described were cis-polypentenamer,[9] cis-polynorbornenamer (of low molecular weight),[10] and in the patent literature cis-polyoctenamer.[11] Polybutenamer has not previously been obtained with more than 60% of its double bonds cis,[12] and polyheptenamer, largely trans and of low molecular weight, has been obtained in only scanty yield.[13,14]

In a typical experiment, a solution of cycloheptene (2.88 g, 30 mmol) in toluene (8.3 g was passed through a column of basic alumina, degassed, and distilled from calcium hydride onto a potassium mirror and then onto (diphenylcarbene)pentacarbonyltungsten (59 mg, 0.12 mmol). The reaction mixture, sealed in a vacuum, was stored at 38° for 36 hr, dissolved in 100 ml toluene, and the product precipitated with methanol yielding 1.9 g (66%) of polyheptenamer. Analyses and results of similar experiments are in table 1.

The polymerization of norbornene was effected in a bottle using 65 g (0.69 mole) and 40 g benzene. The reactants were poured in, purged with argon, the tungsten compound

Table 1. Preparation and Properties of Polyalkenamers

monomer (solvent)[f]	moles olefin/ tungsten	temperature (° C)	time (hr)	yield	$[\eta]$[a] (dl/g)	$\bar{M}_w$[b]	$\bar{M}_n$[b]	% cis	
								Infrared[c]	^{13}C-nmr[d]
cyclobutene (t)	192	rt[e]	15	58	6.54	4.4×10^5	1.7×10^5	93	
cyclopentene (n)	250	40	5.5		4.7			96	95
ditto (n)	500	37	14	40	3.3	3.5×10^5	1.2×10^5	91	80
cycloheptene (t)	250	38	36	66	10.5	1.4×10^6	2.1×10^5	98	>98
cyclooctene (n)	200	40	15	50	10.0			97	
ditto (t)	60	41	14.5	44	3.75	3.7×10^5	2.0×10^5	97	>98
norbornene (b)	168	rt	18	91	7.18	8.5×10^5	3.3×10^5	94	90
ditto (t)	530	rt	72	100	5.90	4.3×10^5	1.0×10^5	95	95

[a] All viscosities were measured at 30° except that of the polyoctenamer prepared in toluene, which was measured at 25° for comparison with the $[\eta]$ - M relationship of a polyocttenamer containing both cis and trans double bonds (reference 15). The solvent was toluene for polypent-, hept-, and octenamers and benzene for polybut- and norbornenamers. [b] Molecular weights were measured by gel permeation chromatography and analyzed by the procedure outlined in footnote 22 of reference 8c. $[\langle L_o^2 \rangle/M]^{1/2}$ for cis-polybutadiene was taken as 0.92 Å. However for polynorbornenamer the molecular weights are estimated as one half those according to polystyrene calibrations. The solvents were THF at ambient temperature for polypent-, hept-, and octenamers, o-dichlorobenzene at 140° for the rest. [c] See note 16. [d] Measured by the ratios of the intensities of the trans and cis C-2 resonances, except for polynorbornenenamer, where the ratio used was that of the resonance at 38.7 to the sum of all resonances from 32 to 44 ppm. [e] Room temperature. [f] t = toluene, n = none, b = benzene.

(201 mg, 0.41 mmol) added, and the bottle capped. After standing overnight the product was dissolved in benzene and precipitated with methanol (see table 1).

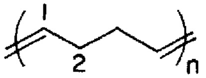
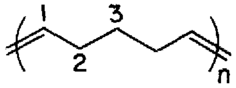
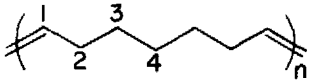
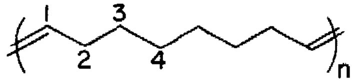
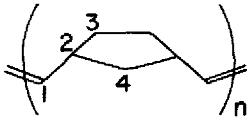
The olefin/tungsten ratio was raised as high as 4000 in one experiment with 150 g norbornene and 50 g pentane. The yield was 67%, $[\eta]$ = 2.56 dl/g, % cis = 95. The ^{13}C-nmr spectra of the polymers are summarized in table 2. The essential point is that trans olefins are characterized by allylic carbon resonances at ca. 5.0 ppm higher frequency than cis,[18] and such resonances are weak or unobserved. The infrared spectra also confirm the stereochemical assignments.[16]

The propensity for forming the cis olefins is we suppose a consequence of conformational factors.[1a,19]

Besides inducing high cis-stereospecificity, the metal-carbene has two other advantages over conventional initiators of olefin metathesis. Since no metalalkyl is present, no acyclic olefins form to decrease molecular weights by chain transfer.[20] And no metal halide is present to induce side reactions of olefins[8b] or to corrode equipment.

That (diphenylcarbene)pentacarbonlytungsten is not the only stable metal-carbene to initiate metatheses is demonstrated by the work in the accompanying paper.[21]

Table 2. ^{13}C-nmr Chemical Shifts of cis-Polyalkenamers in $CDCl_3$ at 60° in ppm Relative to Tetramethylsilane

	C_1	C_2	C_3	C_4	
polybutenamer	129.66	27.52			
polypentenamer	129.91	27.01	29.96		
polyheptenamer	129.88	27.25	29.72	29.02	
polyoctenamer	129.88	27.33	29.85	29.29	
polynorbornenamer	133.95	38.70	33.32	42.77	

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