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METATHESES INDUCED BY (PHENYLMETHOXYCARBENE)PENTACARBONYLTUNGSTEN

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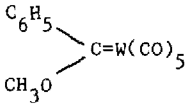
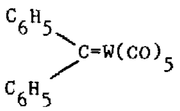
While metal-carbenes should initiate olefin metathesis reactions,[1] the best known, (phenylmethoxycarbene)pentacarbonyltungsten (molecule I),[2,3] has been found not to react with olefinic hydrocarbons.[4,5] However molecule II, the first metal-carbene prepared without stabilizing heteroatoms attached to the carbene center,[6] does,[1,7,8] and since it induces metathesis of a variety of simple cycloalkenes,[1,8] it seemed possible that less active carbenes such as I might initiate the reactions of more active olefins. For this reason, and because the only olefins whose reactions with I had been previously tested, cyclohexene[4a] and tetramethylethylene,[4b] are known to be unresponsive to olefin metathesis,[9,10] we examined whether molecule I would react with the more active cyclobutene and norbornene.



I



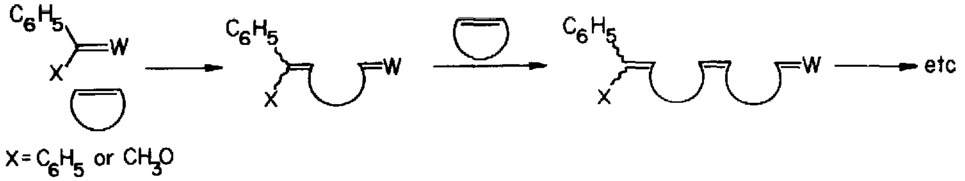
II

The fact is that (phenylmethoxycarbene)pentacarbonyltungsten in small amounts brings about metatheses of both to the corresponding polyalkenamers, and the stereochemistries of the transformations are remarkable.

Thus in experiment 1, norbornene (122g, 1.3 mol) and heptane (80 g) were passed through a column of basic alumina, degassed, and distilled from calcium hydride onto I (563 mg, 1.27 mmol). Heating to 50° for 6 days gave in about 53% yield a polymer that had molecular weights according to gel permeation chromatographic (gpc) analysis[13] $\bar{M}_w = 1.1 \times 10^5$ and $\bar{M}_n = 3.8 \times 10^4$, and that ^{13}C-nmr[14] and infrared analysis[15] showed to be polynorbornenamer 75% of whose double bonds are <u>cis</u>. Similarly cyclobutene (20 mmol), toluene (2 g), and I (47 mg, 0.11 mmol) after 15 hr at 50° gave a rubber that dissolved in benzene and was precipitated by methanol (60% yield), that gpc analysis[16] showed to have molecular weights $\bar{M}_w = 6.0 \times 10^5$ and $\bar{M}_n = 1.7 \times 10^5$, in accord with the intrinsic viscosity,[18] $[\eta] = 4.95$ dl/g in benzene at 30°, and that infrared analysis[19] showed to be polybutadiene 90% of whose double bonds are <u>cis</u>.

If the mechanism by which the metal-carbenes I and II effect metatheses is that indicated in equation 1,[20] the stereochemistries of the resulting polymers should be the same. Indeed both I and II[1] with cyclobutene give polybutenamers whose stereochemistries (*ca.* 90% *cis*) are about the same. But with norbornene the stereochemistries are different. The polynorbornenamer formed by metal-carbene II has 95% of its double bonds *cis*,[1] and that formed in experiment 1 above by metal-carbene I, had only 75% of its double bonds *cis*. This discrepancy is confirmed by repeated experiments. For example, in experiment 2 norbornene (10 g, 106 mmol), toluene (20 g), and I (258 mg, 0.158 mmol) after 4 days at 50° gave in 78% yield polynorbornenamer only about 68% of whose double bonds were *cis*.

In part the difference between the polynorbornenamers formed by I and by II is an illusion, exposed by stirring that formed by I at room temperature with toluene (experiment 1) or with benzene (experiment 2). In either experiment about half the polymer dissolved and about 95% of the double bonds of that half were *cis*. The molecular weights of the polymer that dissolved were determined[21] in experiment 2 as $\bar{M}_w = 1.4 \times 10^5$, $\bar{M}_n = 6.5 \times 10^4$. ($[\eta] = 1.62$ dl/g in benzene at 30°; similarly the first half of the polymer to dissolve in experiment 1 had $[\eta] = 2.31$ dl/g.) The ^{13}C-nmr spectrum was identical with that of the polynorbornenamer formed by initiator II.[1,22] The other half of the polymer formed in experiment 2 when X is CH_3O had molecular weights, $\bar{M}_w = 2.2 \times 10^5$, $\bar{M}_n = 1.0 \times 10^5$,[21] and after extraction with hot benzene (removing another one third of the material), had similar numbers of *cis* and *trans* double bonds.[14] That these are not all in separate chains is indicated by a resonance in the ^{13}C-nmr spectrum 42.1 ppm from TMS,[23] attributable to the one-carbon bridging-methylene between *cis* and *trans* double bonds. The polymer formed by II is similar in that it also exhibits this peak (although less intensely).



(1)

The time and temperature required by I and II to polymerize norbornene are different, and whether these differences or others account for the differences in the polymers has yet to be determined.

The significance of the discovery reported here is that although ways have yet to be found to replace the stabilizing substituents in the metal-carbenes like I in order to transform them into initiators for olefin metathesis, these numerous carbenes themselves might be effective and (phenylmethoxycarbene)pentacarbonyltungsten itself is.

Acknowledgments. We are grateful to Iwao Miura for determining nmr spectra and to David Treatman for determining viscosities.

References and Notes

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(9) For inertness of cyclohexene see (a) G. Dall'Asta and G. Motroni, Angew. Makromol. Chem., **16/17**, 51 (1971); (b) G. Natta, G. Dall'Asta, I. W. Bassi, and G. Carella, Makromol. Chem., **91**, 87 (1966); (c) N. Calderon, J. Macromol. Sci., Rev. Macromol. Chem., **C7**, 105 (1972).

(10) There are no reported metatheses of tetrasubstituted olefins, although there is one report of a reaction with ethylene[11] and two reports of the reverse of that reaction.[12]

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(13) In *o*-dichlorobenzene at 145°. The molecular weights are estimated as one half those according to polystyrene calibrations.

(14) The intensity of the resonance at *ca*. 38.70 ppm[1] divided by the intensities of all non-olefinic carbons times 250. The solvent was *p*-dichlorobenzene + $CDCl_3$ at 92°. See also reference 8c, footnote 18.

(15) See reference 8c, footnote 23.

(16) In *o*-dichlorobenzene at 145°. Molecular weights according to polystyrene calibrations were multiplied by 0.6.[17]

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(20) See references 1 and 8 and others cited there.

(21) Gel permeation chromatographic analysis. See note 13.

(22) The ^{13}C-nmr line widths were 0.14 ppm.

(23) In polynorbornenamer *ca*. 40% of whose double bonds are *cis*[24] the resonance is at 41.45 ppm when the flanking double bonds are both *trans*, 42.18 when one is *cis* and one *trans*, and 42.85 when both are *cis*. The first two resonances are also observed in a polynorbornenamer (formed from $RuCl_3$) 91% of whose double bonds are *trans*.[25]

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