Communications to the Editor

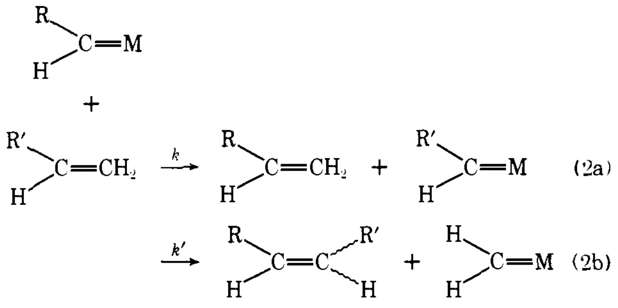
Selectivity in the Olefin Metathesis of Unsymmetrically Substituted Ethylenes

Sir:

With some catalysts terminal olefins undergo the olefin metathesis reaction, eq 1,

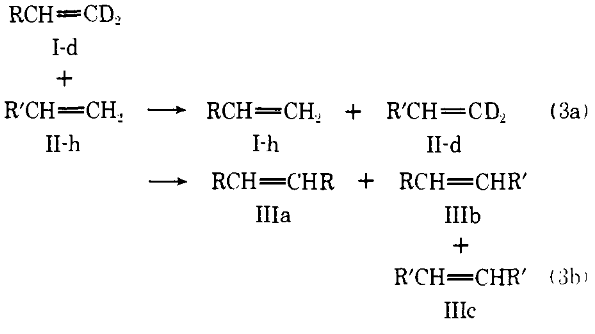
$$2RCH{=}CH_2 \longrightarrow RCH{=}CHR + CH_2{=}CH_2 \quad (1)$$

in only low yield[1,2] while with other catalysts the yields are good.[1a,3] The reasons are neither that terminal olefins are unreactive toward olefin metathesis nor that they are destroyed by side reactions with acids,[1b,c,4] for terminal olefins sometimes do metathesize with internal olefins giving appreciable amounts of all products except those corresponding to eq 1.[1c,2] The possible reasons seem to be either (1) that the metal-carbene complexes combine with terminal olefins selectively according to eq 2a rather than according to eq 2b,[5,6] that this selectivity varies with the catalysts, and that only a limited number of metatheses take place before the chain reactions terminate or (2) that with some catalysts the chain reactions proceed through a greater number of cycles, this number, rather than the selectivity, determining effectiveness.



In this communication we (a) report the first measurements of such selectivity for five catalyst preparations, (b) compare the selectivity in reactions of monosubstituted ethylenes and 1,1-disubstituted ethylenes, (c) report the first soluble catalyst that metathesizes 1,1-disubstituted ethylenes without destroying them in acid-catalyzed side-reactions,[7] and (d) record the first use of an isolable metal-carbene complex without added cocatalyst[3a] as an initiator of olefin metathesis.

Mixtures of 1-octene-*1,1-d*$_2$ (I-d), 1-hexene (II-h), and a normal alkane[8] to serve as an internal standard for GLC analysis were combined with the catalysts, and after a short time reactions were quenched by addition of water. The amounts of III were determined by GLC analysis,[9] and the isotope distributions in I and II by isolating them by GLC[10] and measuring for each by NMR the ratio of protons at positions 1 and 2.



$$\underset{\text{I-d}}{RCH{=}CD_2} + \underset{\text{II-h}}{R'CH{=}CH_2} \longrightarrow \underset{\text{I-h}}{RCH{=}CH_2} + \underset{\text{II-d}}{R'CH{=}CD_2} \quad (3a)$$

$$\longrightarrow \underset{\text{IIIa}}{RCH{=}CHR} + \underset{\text{IIIb}}{RCH{=}CHR'} + \underset{\text{IIIc}}{R'CH{=}CHR'} \quad (3b)$$

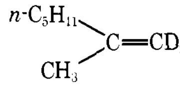
$R = n\text{-}C_6H_{13}$, $R' = n\text{-}C_4H_9$

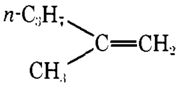
The table summarizes for each catalyst its selectivity, the ratio of the rate constant *k* for reaction 2a (isotopic exchange) and the rate constant *k'* for reaction 2b (conventional metathesis). A similar experiment performed with a mixture of IV and V is also summarized. In making this

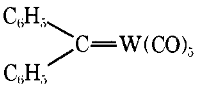
Table I. Ratios of Rate Constants *k* and *k'*

Expt	Reaction	Catalyst	(Mol olefin)/ (g-atoms W or Mo)[a]	Temp (°C)	Reaction time	Fraction metathesis product produced[b,c]	*k/k'* By analysis of hexene	By analysis of octene	Av and standard deviation	Estimated error[d]
1	3	$Mo[(C_6H_5)_3P]_2Cl_2(NO)_2 + (CH_3)_3Al_2Cl_3$[e]	140	0	25 s	0.0451 ± 0.0018	31.8	31.4	26.5 ± 6.1	4.6
2	3		213		11 s	·0.0142 ± 0.0032	19.3	23.4		
3	3	$(C_6H_5)_2C{=}W(CO)_5$	50	50	4.5h	0.0116 ± 0.0017	72.7	77.8	75.2 ± 3.6	12
4	3	$WCl_6 + n\text{-}C_4H_9Li$[f]	51	rt[l]	5 min	0.0073 ± 0.0015	79.0	69.6	80.0 ± 7.8	21
5	3		51		10 min	0.0066 ± 0.0017	87.2	84.4		
6	3	$WCl_6 + (C_6H_5)_3SnC_2H_5$[g]	60	rt[l]	15 min	0.0330 ± 0.0023	130	88	103 ± 20	19
7	3		62		5 min	0.0196 ± 0.0015	96	79		
8	3		61		2 min	0.00218 ± 0.00037	100	121		
9	3	$WCl_6 + C_2H_5OH + C_2H_5AlCl_2$[h]	960	rt[l]	75 s	0.0156 ± 0.0011[i]	203	128	155 ± 33	20
10	3		965		8 s	0.0057 ± 0.0004	153	138		
11	IV + V	$(C_6H_5)_2C{=}W(CO)_5$	36	50	8 h	≤0.0024 ± 0.00035[j]	∞[k]	≥1379[k]	1379 – ∞	355

[a] The g-atomic ratios of Al, Sn, or Li to W or Mo are 10 in experiments 1 and 2, 2 in experiments 4–8, and 4 in experiments 9 and 10. [b] MET in footnote 13. [c] Standard deviations of three analyses, except in experiments 9 and 11 where two analyeses were made. [d] The square root of the sum of the squares of the deviations if the analysis errors are ±2% for NMR and mass spectrometric analyses, ±0.3% for weighing, and the indicated errors for MET. [e] Reference 1a. [f] Reference 4c. [g] Other tin-containing cocatalysts have been used by others: ref 2a, Table 4, and ref 1f. [h] N. Calderon, E. A. Ofstead, J. P. Ward, W. A. Judy, and K. W. Scott, *J. Am. Chem. Soc.*, 90, 4133 (1968). [i] In this one experiment 26% of the hexene and 28% of the octene were lost during the reaction. The average fraction is listed. The losses in the other experiments were much less. [j] No appreciable GLC peaks for products were observed when comparison was made with authentic samples prepared by McMurry's procedure (ref 14). [k] Analysis by low voltage electron impact mass spectrometry. [l] Room temperature.


IV


V


VI

analysis we assumed that the rates of reactions 2a and 2b were unchanged when R and R′ are interchanged, that reaction is effected by those metal-carbenes, RCH=M, in which R = alkyl to the exclusion of those in which R = H,[11] and that the concentration of RCH=M is proportional to the amount of RCH= residue present as olefin.[13]

The observation is that with these catalysts 26–155 methylene interchanges, undetectable except for the isotopic labels, occur for every conventional metathesis. The selectivity is lowest for the molybdenum catalyst most effective for the conventional metathesis of terminal olefins and higher for the less effective tungsten catalysts. Thus the data are in accord with proposal 1 above.

As might reasonably be expected, substituting ethylene twice at the 1-position magnifies the selectivity induced by substituting it only once. To demonstrate this it was impossible to use some of the catalyst mixtures containing WCl_6 or aluminum halides because these acids oligomerize olefins IV and V. However, the isolable metal-carbene VI, which Casey and Burkhardt had cleverly synthesized[15] and found to react stoichiometrically with olefins according to equations similar to 2a,[16] is an effective initiator for metatheses of IV and V as well as of other olefins.[17] Its effectiveness shows that Lewis acid cocatalysts are not essential components of the active catalysts,[5b,18] and that such metal-carbene complexes can be useful in bringing about metathesis of olefins that are very sensitive to acid. An example is in the accompanying paper in which the metathesis selectivity is measured for a trisubstituted olefin.[19]

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References and Notes

(1) (a) E. B. Zuech, W. B. Hughes, D. H. Kubicek, and E. T. Kittleman, *J. Am. Chem. Soc.*, **92**, 528 (1970); (b) A. Uchida, Y. Hamano, Y. Mukai, and S. Matsuda, *Ind. Eng. Chem., Prod. Res. Dev.*, **10**, 372 (1971); (c) T. Zowade and H. Höcker, *Makromol. Chem.*, **165**, 31 (1973); (d) E. L. Muetterties and M. A. Busch, *J. Chem. Soc., Chem. Commun.*, 754 (1974); (e) W. J. Kelly, *Am. Chem. Soc., Div. Pet. Chem., Prepr.*, **17**, H32 (1972); (f) J. Lal and R. R. Smith, *J. Org. Chem.*, **40**, 775 (1975), see peak 2 in Figure 1 and Table III.

(2) (a) See numerous examples in the review by W. B. Hughes, *Organomet. Chem. Synth.*, **1**, 341 (1972), on p 346; (b) J. L. Hérisson and Y. Chauvin, *Makromol. Chem.*, **141**, 161 (1970); (c) V. I. Mar'in, A. D. Shebaldova, T. A. Bol'shinskova, M. L. Khidekel', and I. V. Kalechits, *Kinet. Catal. (USSR)*, **14**, 528 (1973).

(3) (a) W. R. Kroll and G. Doyle, *Chem. Commun.*, 839 (1971), *J. Catal.*, **24**, 356 (1972); (b) G. Doyle, *ibid.*, **30**, 118 (1973); (c) N. S. Nametkin et al., *Dokl. Chem.*, **213**, 872 (1973); (d) G. Descotes, P. Chevalier, and D. Sinou, *Synthesis*, 364 (1974); (e) many examples effected with heterogeneous catalysts were reviewed by G. C. Banks, *Catal. Rev.*, **3**, 37 (1969).

(4) (a) R. Wolovsky, N. Moaz, and Z. Nir, *Synthesis*, **2**, 656 (1970); (b) J. R. Graham and L. H. Slaugh, *Tetrahedron Lett.*, 787 (1971); (c) J.-L. Wang and H. R. Menapace, *J. Org. Chem.*, **33**, 3794 (1968).

(5) (a) T. J. Katz and J. McGinnis, *J. Am. Chem. Soc.*, **97**, 1592 (1975); (b) E. L. Muetterties, *Inorg. Chem.*, **14**, 951 (1975).

(6) W. J. Kelly and N. Calderon, *J. Macromol. Sci. Chem.*, **9**, 911 (1975), found scrambling between 1-pentene and 1-pentene-d_{10}.

(7) There are heterogeneous catalysts: (a) A. M. Popov et al., *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, **22**, 1397 (1973); (b) R. L. Banks and R. B. Regier, *Ind. Eng. Chem., Prod. Res. Dev.*, **10**, 46 (1971); (c) L. F. Heckelsberg, Belgium Patent, 713 184 (1967); (d) H. Knoche, German Patent, 2 024 835 (1970); *Chem. Abstr.*, **74**, P44118 (1971); (e) for the reverse reaction: D. L. Crain, *J. Catal.*, **13**, 110 (1969).

(8) *n*-Heptane for experiments 3 and 6–11, *n*-nonane for experiments 4 and 5, and *n*-hexadecane for experiments 1 and 2.

(9) 10 ft × ⅛ in. 20% Apiezon L on Chromosorb W Regular.

(10) Same as 9, but Apiezon J and ¼ in.

(11) The experiments by Casey, Tuinstra, and Saemen in the accompanying manuscript support this assumption and measure in a different way selectivities similar to those recorded here.[12]

(12) C. P. Casey, H. E. Tuinstra, and M. Saemen, *J. Am. Chem. Soc.*, **98**, 608 (1976).

(13) With HEX, OCT, and OCTO representing the number of protons at positions 1 in hexene, octene, and "octene-d_2", R the molar ratio of hexene and octene, and MET the molar ratio (IIIa + IIIb + IIIc)/(I + II),

$$\frac{k}{k'} = (-1/\mathrm{MET}) \ln \left[1 - \left(\frac{2 - \mathrm{HEX}}{2 - \mathrm{OCTO}} \right) (1 + R) \right]$$

or

$$(1/\mathrm{MET}) \ln \left[\frac{1 - [\mathrm{OCTO}(1 + R)/(2R + \mathrm{OCTO})]}{1 - [\mathrm{OCT}(1 + R)/(2R + \mathrm{OCTO})]} \right]$$

(14) J. E. McMurry and M. P. Fleming, *J. Am. Chem. Soc.*, **96**, 4708 (1974).

(15) C. P. Casey and T. J. Burkhardt, *J. Am. Chem. Soc.*, **95**, 5833 (1973).

(16) C. P. Casey and T. J. Burkhardt, *J. Am. Chem. Soc.*, **96**, 7808 (1974).

(17) 2-Hexene for example.

(18) H. Höcker and F. R. Jones, *Makromol. Chem.*, **161**, 251 (1972).

(19) T. J. Katz, J. McGinnis, and C. Altus, *J. Am. Chem. Soc.*, **98**, 606 (1976).

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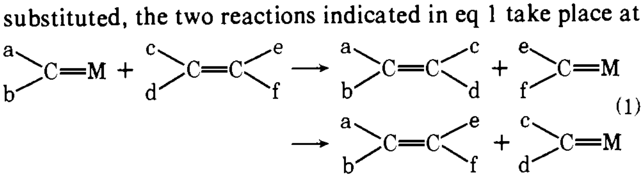
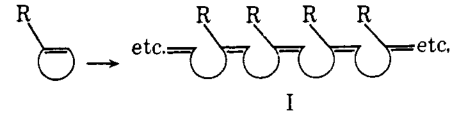
Metathesis of a Cyclic Trisubstituted Alkene. Preparation of Polyisoprene from 1-Methylcyclobutene

Sir:

When metal-carbene complexes combine in the olefin metathesis reaction[1] with olefins that are unsymmetrically substituted, the two reactions indicated in eq 1 take place at different rates.[2,4] This accounts for the selective formation of oligomers whose structures may be represented as $RCH{=}\sim\!\sim\!\sim{=}CH_2$ in reactions of cycloolefins with terminal acyclic olefins[2] and for the selective formation of starting olefins in reactions of terminal olefins with themselves.[4a]


(1)

If this selectivity also applied to trisubstituted olefins, a predicted consequence (eq 2) would be that cycloalkenes unsymmetrically substituted on the double bond would yield polymers that, except possibly for geometrical isomerism, are translationally invariant. Such polymers are said to be "perfectly alternating".[5] To test this prediction a way must be found to effect metatheses of olefins that are trisubstituted. We report below a solution to the problem, the preparation by metathesis of a polymer from a cyclic trisubstituted alkene, and an analysis of the metathesis selectivity.



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(2)

A number of years ago Dall'Asta and Manetti tried to polymerize 1-methylcyclobutene with WCl_6 and either triethylaluminum or ethylaluminum dichloride, but the polymers produced were largely saturated.[6] With similar catalyst mixtures trimethylethylene gives olefin oligomers,[7] although 2-methyl-2-pentene is said to give the expected metathesis products.[8]

Other metathesis catalysts are also ineffective. The combination of $MoCl_2(NO)_2[(C_6H_5)_3P]_2$ and $(CH_3)_3Al_2Cl_3$ in chlorobenzene at room temperature[9] with both 1-methylcyclobutene[10] for 18 h[11] and 1-methylcyclopentene for 2 h gives products shown by their proton NMR spectra to be too saturated to contain structures like I in quantity.[12] WCl_6 and $(C_6H_5)_3SnC_2H_5$ in chlorobenzene at room temperature[4a] for 3 h[13] with 1-methylcyclobutene gives some-