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INDUCTION OF OLEFIN METATHESIS BY ACETYLENES.(U)
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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
Technical Report, No. 2, 1 Aug 79-20		NR 842
4. TITLE (and Subtitle)	5. TYPE OF REPORT & PERIOD COVERED	
Induction of Olefin Metathesis by Acetylenes.	Technical Report, 8/1/79-11/20/80	
	6. PERFORMING ORG. REPORT NUMBER	
7. AUTHOR(s)	8. CONTRACT OR GRANT NUMBER(s)	
Thomas J. Katz, Steven J. Lee, Mridula Nair, and Edward B. Savage	NO0014-79-C-0683	
9. PERFORMING ORGANIZATION NAME AND ADDRESS		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
Thomas J. Katz Chemistry Department Columbia University, New York, N.Y. 10027		NR 356-726
11. CONTROLLING OFFICE NAME AND ADDRESS		12. REPORT DATE
Office of Naval Research - Chemistry Arlington, VA 22217		11/20 November 20, 1980
13. NUMBER OF PAGES		14. SECURITY CLASS. (of this report)
14		Unclassified
15. DECLASSIFICATION/DOWNGRADING SCHEDULE		
16. DISTRIBUTION STATEMENT (of this Report)		
This document has been approved for public release. Distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
To be published in the <u>Journal of the American Chemical Society</u>		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number)		
Polymers	Metathesis	Alkenes
Polymerization	Metal-carbenes	Alkynes
Catalysis	Polyacetylenes	
Initiation	Polyalkenamers	
20. ABSTRACT (Continue on reverse side if necessary and identify by block number)		
Acetylenes induce (phenylmethoxycarbene)pentacarbonyltungsten to initiate metatheses of cis-2-pentene, cyclooctene, cycloheptene, and cyclopentene, but too much quenches the reactions. The first three of these transformations are remarkably stereoselective, yielding olefins that are 94 to 97% cis. These observations accord with the hypothesis that Scheme 1 is the mechanism of acetylene polymerization. They also provide a functional equivalent (an acetylene) of the organometallic cocatalysts like ethylaluminum dichloride, unique in operating in the absence of strong Lewis acid metal-halides.		

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Task No. NR 356-726

TECHNICAL REPORT NO. 2

Induction of Olefin Metathesis by Acetylenes

by

Thomas J. Katz, Steven J. Lee, Mridula Nair and Edward B. Savage

Prepared for Publication

in the

Journal of The American Chemical Society

Columbia University
Department of Chemistry
New York, New York

November 20, 1980

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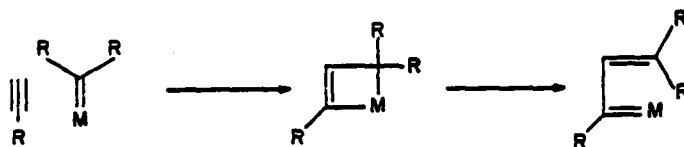
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Induction of Olefin Metathesis by Acetylenes

Sir:

If the reason that metal-carbenes polymerize acetylenes¹ is because the transformations involve the steps in Scheme 1,^{1,2} then combining metal-

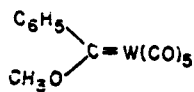
Scheme 1



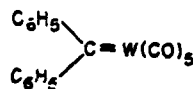
carbenes and acetylenes should generate other, possibly more reactive metal-carbenes that might initiate transformations their precursors could not. We recently discovered that acetylenes can induce olefin metatheses,^{3,4} and we are reporting here how the process can be made to work generally, and remarkably stereospecifically. We have discovered that acetylenes not only induce the reactions, but quench them as well, and in an accompanying paper we analyze why.⁵

Table 1 shows that if 200 equivalents of three cycloalkenes are combined with 1 equivalent of (phenylmethoxycarbene)pentacarbonyltungsten 1,⁶ no polyalkenamers^{1a,7} form, but that if phenylacetylene is present, the reactions (eq 1) do indeed take place, even if slowly. However, preliminary attempts to effect the analogous transformation with the seemingly related molecule cis-2-pentene were ineffective, even when ever larger amounts of acetylenes and large amounts of metal-carbenes were used.

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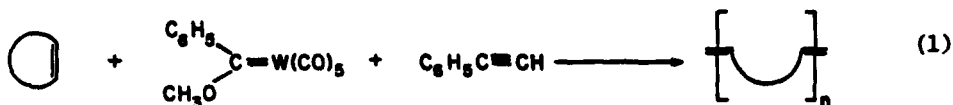


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as initiators. Thus 200 equivalents of phenylacetylene and 7 of 1 after 6



days at 50 °C converted 160 equivalents of cis-2-pentene into less than half an equivalent of the butenes plus hexenes although 67% of the phenylacetylene was transformed and isolated as its polymer.

The key to bringing about the reactions more efficiently, it turns out, is to use less (not more) of the acetylene. Fig. 1 illustrates this for combinations of cyclopentene (100 equiv.), phenylacetylene (varying amounts), and metal-carbene 1 (1 equivalent), for it shows that the inverse of the yield of polypentenamer increases linearly with the concentration of phenylacetylene.⁸ Notice according to this graph, that to achieve a 100% yield, one simply has to use no phenylacetylene at all!

Similar increases in yields with decreasing acetylene concentration have been measured for other olefins and are illustrated by the enhanced rates of conversion (compared to the ones described above) in Table 2.

Table 1. Yields of Polyalkenamers obtained in Metatheses Induced by Combining Cycloalkenes (200 equiv.), Phenylacetylene (10 equiv.), and Metal-Carbenes **1** (1 equiv.) at 50 °C.^a

Cycloalkene ^b	Time (days)	Yield ^{c,d} (%)
5	7	19
7	13	16
8	24	7

^a In the absence of phenylacetylene, the three cycloalkenes after 7, 26, and 24 days respectively gave no polyalkenamers. ^b Number of carbons. ^c The yields are those of the polyalkenamers isolated by dissolving the reaction products in CH₂Cl₂, precipitating with CH₃OH, and drying in a vacuum. They may be in error by ca. 20% (relative). ^d After 5 days neither cycloheptene nor cyclooctene polymerized appreciably (< ca. 6%), for the reaction mixtures were not yet significantly viscous.

Table 2. Yields and Molecular Weights of Products Obtained in Metatheses Induced by Combining Olefins (100 equiv.), Phenylacetylene (1 equiv.), and Metal-Carbene **1** (1 equiv.) at 50 °C.

Olefin	Time (days)	Yield (%)	$\bar{M}_w^a$ x10 ⁻³	$\bar{M}_n^a$ x10 ⁻³
cycloheptene	2	16 ^b	321	135
cyclooctene	3.5	8 ^b	281	147
cis-2-pentene	7	7.9 ^c		

^a Molecular weights were analyzed by gel permeation chromatography in toluene on Waters Associates μ -styrigel. The values recorded are half the weights of the polystyrenes that would exhibit the chromatograms observed (see references 5 and 9). ^b $\pm$ ca. 20% (relative). ^c 100 (moles butene + moles hexene)/moles pentene. The error is ca. 4% (relative).

These metatheses can be very highly stereoselective.¹⁰ For cycloheptene (IR analysis:¹¹ 97±1% cis, ¹³CNMR:¹² >96%),¹⁴ cyclooctene (IR: 94.3±2% cis, ¹³CNMR: 94±1%),¹⁵ and cis-2-pentene (the 2-butenes are 96.5±0.6% cis, the 3-hexenes 93.7±0.8% cis),¹⁸ although not for cyclopentene (IR: 74±8% cis, ¹³CMR: 58%),²⁰ the stereoselectivities are substantially higher than for every other initiator previously studied, with one significant exception, (diphenylcarbene)pentacarbonyltungsten (2).^{9,19} This is a remarkable observation, yet it agrees with the introductory premises because the effect of the transformation in Scheme 1 is to convert metal-carbene 1 into a substance whose structure is essentially that of 2. The acetylene is thus an activator, but unlike the organometallic co-catalysts like C₂H₅AlCl₂, which it replaces, it is unique in operating in the absence of strong Lewis acid metal-halides, whose presence may account for why most metatheses are only weakly stereoselective^{19,21} and for why some are accompanied by undesirable side-reactions.²²

The observation that acetylenes induce metatheses supports the idea that acetylene polymerization like olefin metathesis involves the addition of metal-carbenes to carbon-carbon multiple bonds. The observation that acetylenes quench metatheses too is also in accord with the hypothesis as analyzed in the following paper.⁵

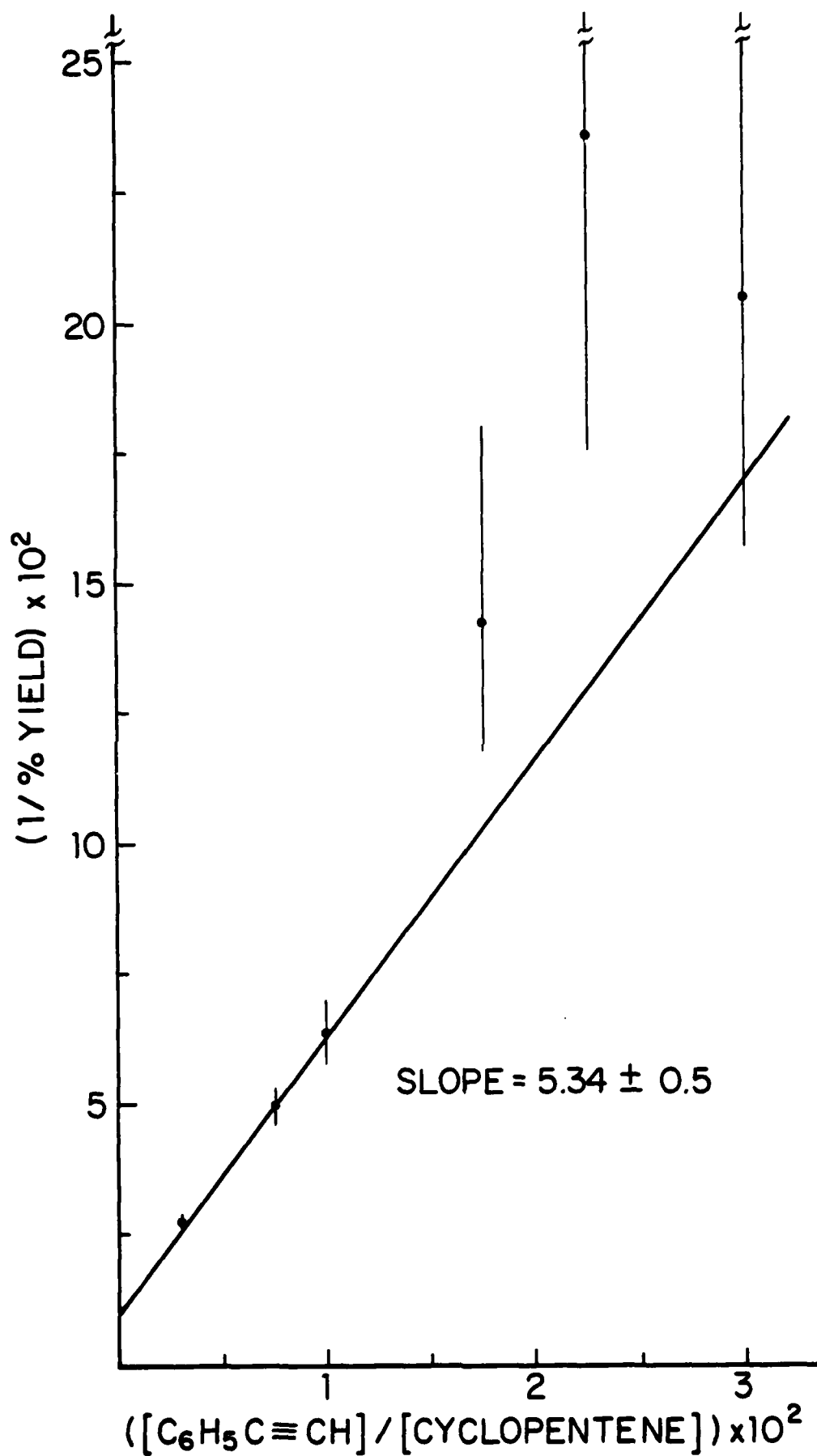
Acknowledgment. We are grateful for the support of the National Science Foundation (CHE-77-22726) and the U.S. Office of Naval Research.

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Figure Caption

Figure 1. Inverse of the yield of polypentenamer as a function of the ratio of phenylacetylene and cyclopentene. Cyclopentene (100 equiv.), phenylacetylene (varying amounts), and I_2 (1 equiv.) were combined at 50 °C for 21.5 h. The bars show the errors introduced if the weight of the polymer obtained from 680 mg of cyclopentene is measured incorrectly by 10 mg. The yield (100%) at [phenylacetylene] = 0 is derived from theory (see reference 5). The slope and standard deviation are those of the least squares straight line through the first four points, weighted as the inverses of the relative errors in the inverse yields. The last three points were discarded because when the yields and molecular weights are low, the fraction of polymer lost in the isolation can be high. (These points therefore all appear above the line.)

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- (11) Measured by the ratio of the intensities of the infrared peaks at ca. 1400 and 960 cm^{-1} . See reference 9, footnote 16.
- (12) The intensities of the trans and cis C-2 resonances (see reference 9, the references in its footnote 18, and reference 13) were measured, and for polyoctenamer those of the two olefinic carbon resonances as well.
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- (15) WCl_6 (or in one case a tungsten-carbene) + organoaluminum compounds have given polyoctenamers that are largely trans.^{14a,b,16} At low temperatures in the presence of certain modifiers [$\text{BF}_3 \cdot (\text{C}_2\text{H}_5)_2\text{O}$ at -30°C or diisobutylaluminum oxide at $+12^\circ\text{C}$] or when WF_6 is used in place of WCl_6 , the polymer formed is said to be largely cis.¹⁷
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