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EXPLORATORY HIGH PRESSURE CHEMISTRY.(U)
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FINAL REPORT

EXPLORATORY HIGH PRESSURE CHEMISTRY

JOHN A. GLADYSZ

AFOSR-79-0092

UNIVERSITY OF CALIFORNIA, LOS ANGELES
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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER AFOSR-TR- 82 - 0522	2. GOVT ACCESSION NO. <i>11 June 79</i>	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Exploratory High Pressure Chemistry		5. TYPE OF REPORT & PERIOD COVERED Final
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) John A. Gladysz		8. CONTRACT OR GRANT NUMBER(s) AFOSR-79-0092
9. PERFORMING ORGANIZATION NAME AND ADDRESS University of California, Los Angeles Department of Chemistry Los Angeles, California 90024		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 61102F 2303/B2
11. CONTROLLING OFFICE NAME AND ADDRESS Air Force Office of Scientific Research/NC Bolling Air Force Base, D.C. 20332		12. REPORT DATE 1 April 1979 - 31 March 1982
		13. NUMBER OF PAGES 9
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) UNCLASSIFIED
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary, and identify by block number) Silatropic Shift Cycloaddition Pressure Migratory Insertion		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) A novel 1,3-silatropic shift was observed in the acylation of a silylated iron anion. A high yield cycloaddition of allyl iron complexes to olefins under pressure was carried out. This reaction constitutes a relatively rare example of a 3 plus 2 cycloaddition to give a 5-membered carbocyclic ring. It was found that migratory insertion reactions of transition metal alkyls can be effected by the application of pressure.		

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FINAL TECHNICAL REPORT
 April 1, 1979 - March 31, 1982
 Grant AFOSR - 79-0092
 J.A. Gladysz
 Principal Investigator
 Department of Chemistry
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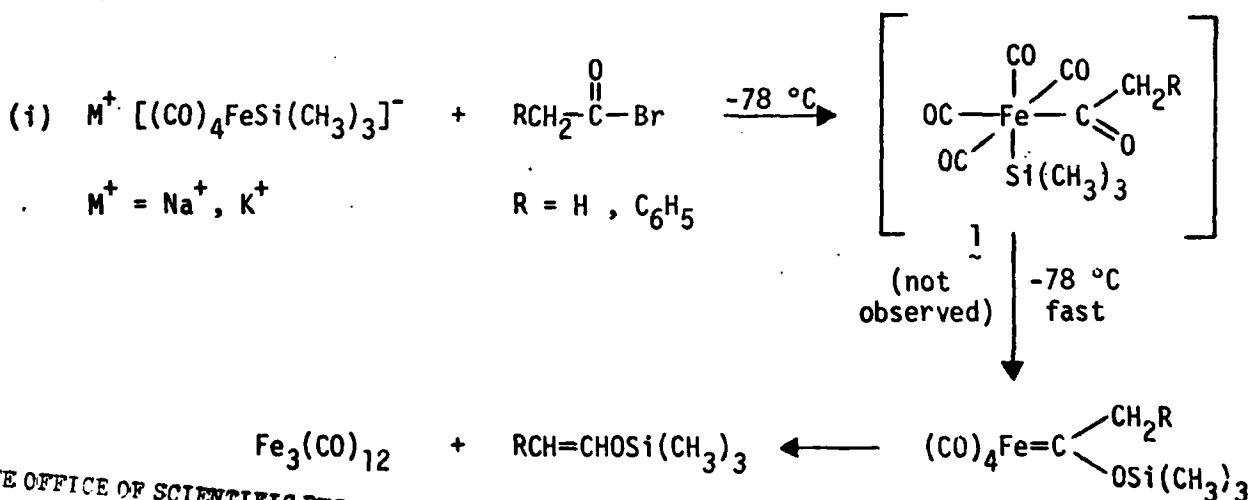
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Most of the research described in this report deals with high pressure organic and organometallic chemistry. However, due to some difficulties encountered in pursuing this line of research (caused in part by the deaths of two key collaborators, Professors William F. Libby and George Kennedy, during the course of this project; they furnished the host laboratory), the scope of the project was expanded (following consultation with Dr. Matuszko) to include studies of organosilicon and metal/silicon compounds.

I. 1,3-Silatropic Shifts from Iron to Acyl Oxygen

We have completed a study of the acylation of the silylated iron anion $M^+ [(CO)_4FeSi(CH_3)_3]^-$ ($M^+ = Na^+, K^+$).¹ We anticipated formation of acyl intermediates 1 (eq i), and hoped that 1 might eliminate an acyl silane. However, 1 did not prove detectable at $-78^\circ C$. Instead, a novel 1,3-silatropic shift occurred to give the carbenes $(CO)_4Fe=C(R)OSi(CH_3)_3$ 2. These have been characterized by 1H NMR, ^{13}C NMR, and IR. Upon standing at $25^\circ C$, they convert (via a hydride shift) to silyl enol ethers. This work is being submitted to Organometallics for publication.

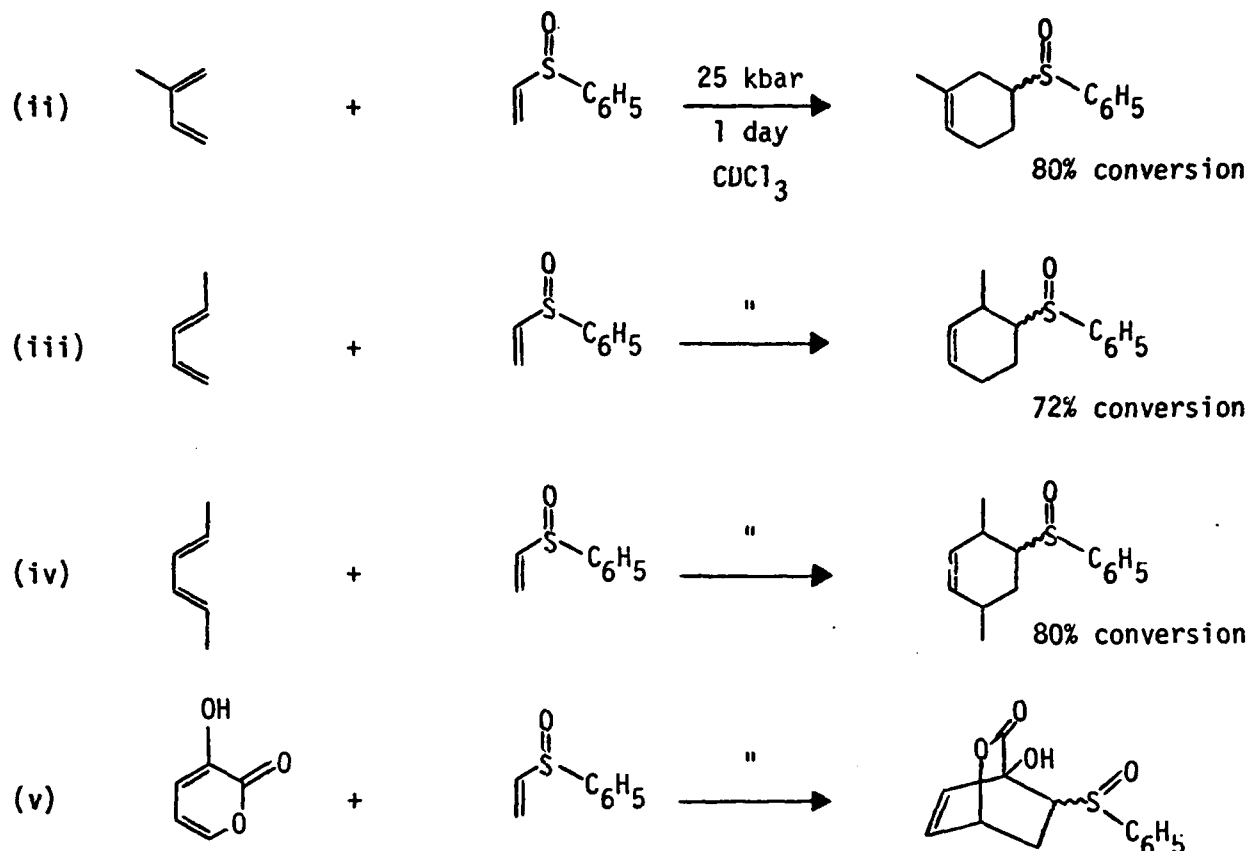


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II. Vinyl Sulfoxide Cycloadditions

We have successfully executed the following cycloadditions of phenyl vinyl sulfoxide:

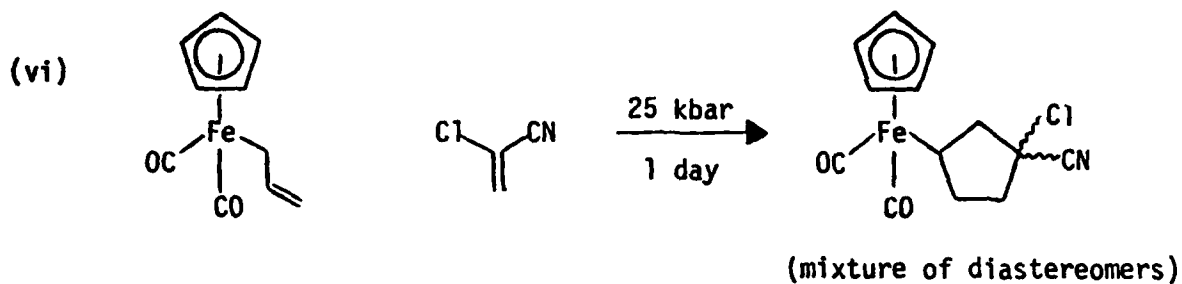


Normally cycloadditions of phenyl vinyl sulfoxide require such high temperatures that extrusion of $\text{C}_6\text{H}_5\text{SOH}$ (and concomitant olefin formation) occurs.² In the above reactions, the sulfoxide group is retained, which provides a convenient handle for carbon-carbon bond forming reactions and other functionality transformations. The products in eq iii-v are obtained as diastereomer mixtures; upon heating, $\text{C}_6\text{H}_5\text{SOH}$ eliminates and previously synthesized² dienes form.

III. Cycloadditions of Iron Complexes

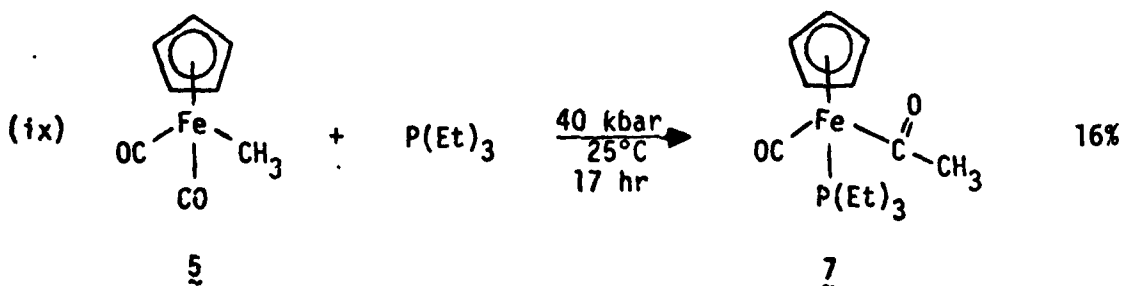
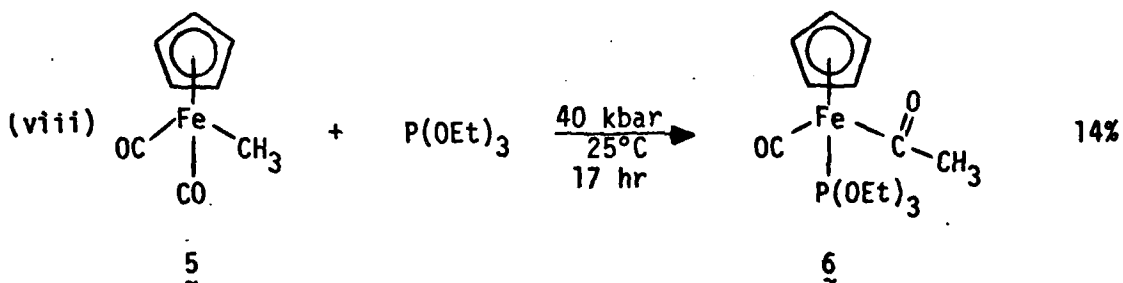
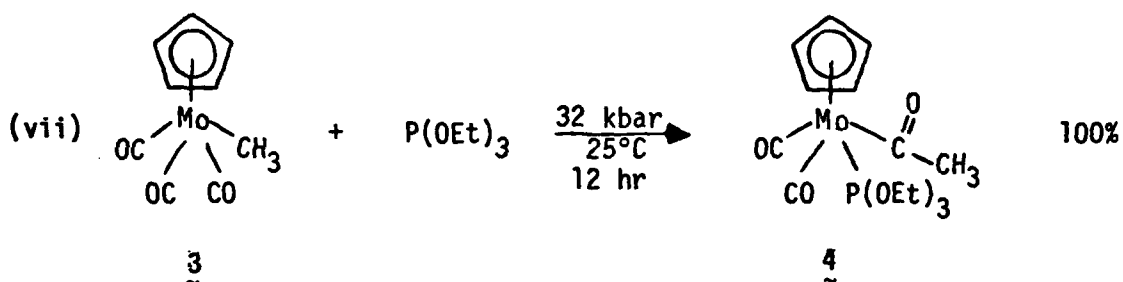
We have been able to effect the high yield cycloaddition of allyl iron complexes to olefins under pressure, as shown in eq vi. This type of cyclopentane forming reaction was previously possible only with the highly electron deficient diene TCNE.³ We have also been able to execute similar cycloadditions with

acrylonitrile and α -(phenylthio)acrylonitrile. This reaction constitutes a relatively rare example of 3+2 cycloaddition to give a 5-membered carbocyclic ring.

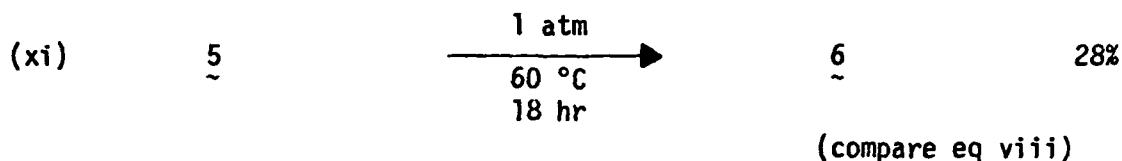
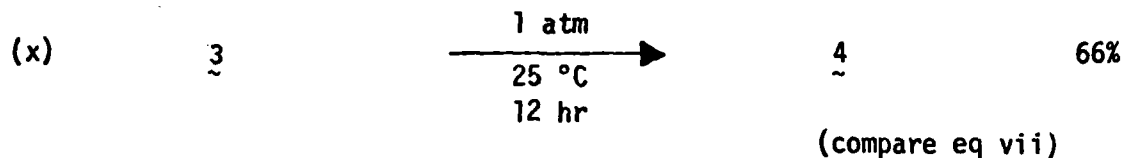


IV. "Migratory Insertion" Reactions

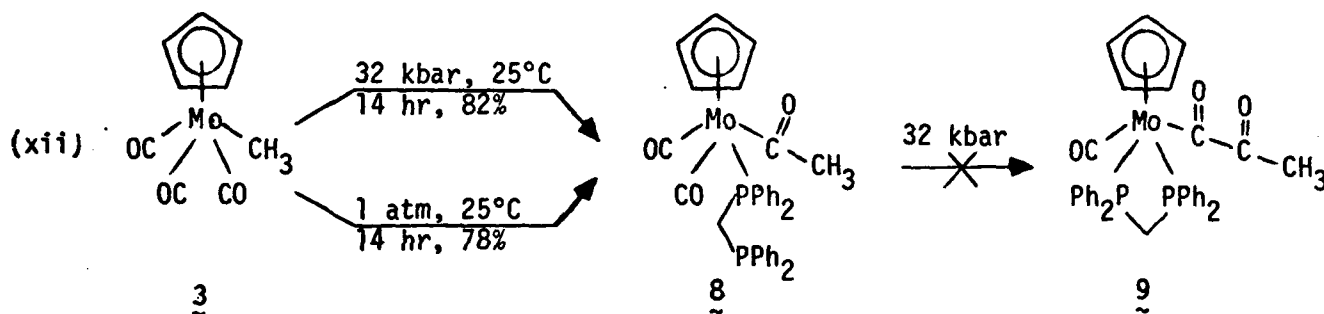
We have found that "migratory insertion" reactions of transition metal alkyls can be effected by the application of pressure:



Literature conditions for reactions vii-ix indicate that temperatures of 80-120 °C are required⁴ at 1 atm. However, our control reactions gave the following results:



Thus, in a preparative sense, pressure only mildly accelerates rates of "migratory insertions" of transition metal alkyls. Hence $\Delta V^\ddagger$ is probably only slightly negative. We attempted to achieve a "multiple" insertion with 3 and $\text{Ph}_2\text{PCH}_2\text{PPh}_2$; however, the target molecule 9 was not obtained, and the thermal, 1 atm reaction yielded identical results (eq xii).



V. Uranium - Silicon Compounds

Compounds with uranium-silicon bonds have not previously been prepared. These may have useful properties for uranium isotope separation, so we have embarked upon some exploratory studies. We have attempted to use the zirconium silane 10 (eq xiii), the synthesis of which we have recently reported,⁵ as a trimethylsilyl transfer agent:

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- (1) "High Pressure Cycloadditions of Pyrones; Synthesis of Highly Functionalized Six-Membered Rings by Inhibition of Carbon Dioxide Loss," J.A. Gladysz, S.J. Lee, J.A.V. Tomasello, and Y.S. Yu, *J. Org. Chem.*, **42**, 4179 (1977).
- (2) "Ene Reactions of β -Pinene at Room Temperature and 40 kbar Pressure," J.A. Gladysz and Y.S. Yu, *J. Chem. Soc., Chem. Commun.*, 599 (1978).
- (3) "Squeezing the Transition State," J.A. Gladysz, *CHEMTECH*, **9**, 372 (1979).
- (4) "Alkylation and Acylation of the $[(CO)_4FeSi(CH_3)_3]^-$ Anion; A Novel 1,3-Sigmatropic Shift from Iron to Acyl Oxygen," A.J. Blakeney, W. Krone-Schmidt, and J.A. Gladysz, in preparation for Organometallics.

Public Lectures Based Upon This Project

- (1) University of Idaho, Moscow, Idaho, "Organic Reactions Under Extreme Conditions: From Hot Atoms to 50,000 Atmospheres," April 19, 1979.
- (2) G.D. Searle & Co., Chicago, Illinois, "I. Synthetic Chemistry under 20-40 Kbar Pressure; II. New Methods of Asymmetric Organic Synthesis; 100% Chirality Transfer from Rhenium to Carbon," March 28, 1980.
- (3) Exxon Research and Engineering, Linden, New Jersey, "Organic Reactions Under Extreme Conditions: From Hot Atoms to 50,000 Atmospheres," March 1, 1982.
- (4) 28th Congress of the International Union of Pure and Applied Chemistry, Vancouver, Canada, "Organic Chemistry Under Extreme Conditions: Hot Atoms to 50,000 Atmospheres," August 18, 1981.

Coworkers On This Project

- (1) Postdoctoral: Dr. Bong-Rae Cho
- (2) Graduate Student: Mr. Wilfried Krone-Schmidt
A portion of Wilfried's Ph.D. thesis will be based upon this project.
- (3) Undergraduate Students: Mr. David Parker
Mr. Ron Ugolick
Mr. Yeung Yu
Mr. Jim Tomasello
Mr. Sung Lee